NATIONAL
URANIUM
TAILINGS
PROGRAM

Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

Canada

STUDY OF THE STATE
OF NICKEL AND ARSENIC
IN URANIUM MILL TAILINGS
ADDENDUM REPORT
MARCH, 1987

DSS File No. 15 SQ-23327-6-1727

CONTRACT REPORT NO. 61727-01-SQ

MCEL PROJECT NO. 115-A

prepared for

Department of Energy, Mines and Resources
Canada Centre for Mineral and Energy Technology
National Uranium Tailings Program

by

36 pp

MELIS CONSULTING ENGINEERS LTD.
519 45TH Street West
SASKATOON, Saskatchewan, Canada

MICROMEDIA

MELIS CONSULTING ENGINEERS LTD.
519 45th Street West
Saskatoon, Saskatchewan, Canada
S7L 5Z9
(306) 652-4084
Telex: 074-2683 (NORPLEX)

March 31, 1987

Dept. of Energy, Mines and Resources
CANMET
555 Booth Street
OTTAWA, Ontario
K1A 0G1

MCEL Project No.115-A

Attention: Dr. C.W. Smith

Dear Dr. Smith:

re: File No. 15 SQ-23327-6-1727
Nickel-Arsenic Study-Addendum

Please find enclosed twenty (20) copies of the final report entitled "Study of the State of Nickel and Arsenic in Uranium Mill Tailings - Addendum Report". This report summarizes the work carried out as an extension of the original study completed in 1986 for the National Uranium Tailings Program.

We trust the results of these additional studies prove useful to the National Uranium Tailings Program. Melis Consulting Engineers Ltd. appreciates the opportunity of being of service to the Department of Energy, Mines and Resources and we remain available to discuss any aspect of our work at your convenience.

Respectfully submitted,
MELIS CONSULTING ENGINEERS LTD.

L.A. Melis

L.A. Melis, P.Eng.
Principal

LAM:dm
enclosures

STUDY OF THE STATE
OF NICKEL AND ARSENIC
IN URANIUM MILL TAILINGS
ADDENDUM REPORT

TABLE OF CONTENTS

		Page No.
1.0	SUMMARY	1
2.0	INTRODUCTION	3
3.0	SAMPLE DESCRIPTION	4
4.0	RAFFINATE NEUTRALIZATION TESTS	7
	4.1 Methodology	7
	4.2 Results	7
5.0	WASTE TREATMENT SIMULATION TEST	13
	5.1 Methodology	13
	5.2 Results	13
6.0	PREPARATION AND EXAMINATION OF IRON ARSENATES	16
	6.1 Preparation	16
	6.2 X-Ray Diffraction Analysis	18
7.0	SYNTHETIC SOLUTION TEST	23
8.0	IRON AND ARSENIC SPECIATION ANALYSIS	24
9.0	ANALYTICAL METHODOLOGY	26
	9.1 Quality Control	26
	9.2 Radiochemical Analysis	26
APPENDIX A	Original Statement of Work	

STUDY OF THE STATE
OF NICKEL AND ARSENIC
IN URANIUM MILL TAILINGS
ADDENDUM REPORT

LIST OF TABLES

Table No.	Description	Page No.
3-1	Assessment of Original Key Lake Waste Solution Samples	5
3-2	Analysis of Fresh Raffinate Sample	6
4-1	Raffinate Neutralization Results	8
5-1	Key Lake Waste Treatment Simulation Test Conditions	14
5-2	Key Lake Waste Treatment Simulation Test Results	15
6-1	Iron Arsenates Weight Loss Comparison	19
8-1	Iron and Arsenic Speciations Analysis-Key Lake Solvent Extraction Raffinate	25

LIST OF FIGURES

Figure No.	Description	
4-1	Raffinate Neutralization Tests - Radium-226 Profile	9
4-2	Raffinate Neutralization Tests - Thorium-230 Profile	10
4-3	Raffinate Neutralization Tests - Uranium Profile	11
4-4	Raffinate Neutralization Tests - Precipitate Weight Profile	12
6-1	Iron Arsenate Precipitates - X-ray Diffraction Patterns	20
6-2	Iron Arsenate Precipitates - X-ray Diffraction Patterns	21

STUDY OF THE STATE
OF NICKEL AND ARSENIC
IN URANIUM MILL TAILINGS

1.0 SUMMARY

Additional investigations were carried out on Key Lake mill waste solutions as a result of an original study on the state of nickel and arsenic in uranium mill tailings (MCEL Project No. 115, August, 1986 Report).

Solvent extraction raffinate neutralization tests at various pH levels showed that partial radium precipitation occurs with the addition of lime only. Thorium removal to acceptable levels is complete at pH 7 and uranium removal to trace levels is complete at pH 3.5.

A simulation test of the Key Lake waste treatment circuit was repeated to investigate the deportment of radionuclides in the final treated filtrate and in the waste precipitates.

Ferrous and ferric arsenates were prepared by sodium hydroxide neutralization of arsenate solution. The iron arsenate precipitates were subsequently heated to various temperatures, from 110°C to 500°C, in an attempt to simulate accelerated aging of the precipitates. X-ray diffraction analysis showed that the heated precipitates were still present as amorphous solids without any crystal structure. Thenardite, sodium sulphate, was the only crystalline mineral observed.

Synthetic solution tests were completed to investigate the co-precipitation of arsenic with ferrous and ferric sulphate. The filtrate analysis from these tests indicated a lower arsenic assay for the ferrous test (0.069 g/L As) than for the ferric test (0.24 g/L As). This result strongly suggests that ferrous iron plays an important role in the precipitation of arsenic from solution.

Iron and arsenic speciation analysis of three separate Key Lake solvent extraction raffinate samples gave an arsenate to arsenite ratio of 2:1 and a ferric to ferrous ratio of 1:7. The high ferrous content of the Key Lake raffinate indicates that ferrous iron plays an important role in the removal of arsenic from Key Lake waste solution.

2.0 INTRODUCTION

The initial study completed for the National Uranium Tailings Program on the state of nickel and arsenic in uranium mill tailings (MCEL Project No. 115, August, 1986 Report) led to recommendations for follow-up work. The further investigations requested by the National Uranium Tailings Program office are itemized in the Statement of Work attached in Appendix A.

The work scope for the addendum program included the following:

- repeat the batch-liming experiments with Key lake raffinate at various pH levels and follow the radionuclide distribution in the filtrate and precipitate products for all experiments, analyse for iron and lead in the filtrate solutions, and analyse for nickel and arsenic in the pH 3.5 sample
- repeat the Key Lake waste treatment circuit simulation test and follow the radionuclide distribution in the final products
- prepare synthetic ferrous and ferric arsenate compounds, heat these two compounds to various temperatures in a nitrogen atmosphere and analyse the resulting products by X-ray diffraction
- repeat the arsenic/aluminum synthetic solution test but replace aluminum with ferrous and ferric iron
- obtain arsenic and iron speciation analysis on different samples of Key Lake raffinate.

This addendum work was carried out by Melis Consulting Engineers Ltd. using the Saskatchewan Research Council (SRC) facilities in Saskatoon, Saskatchewan. The work was completed during January and February, 1987.

3.0 SAMPLE DESCRIPTION

The four Key Lake waste stream solutions used in the initial testwork were examined for evidence of precipitation prior to initiating the addendum testwork. A 2 L sample of each liquid; minewater, solvent extraction raffinate, spent regeneration solution and tailings pond seepage and supernatant, was filtered and the collected suspended solids were dried, weighed and analysed for radionuclide content. The results of this investigation are tabulated in Table 3-1.

From these results it was noted that suspended solids were observed in all four liquids but only the solids collected from the raffinate sample contained a substantially high level of radium. Thorium-230 and uranium analyses were not possible due to the small amount of solids available for analysis. From the low level of radium observed in the raffinate filtrate (9 Bq/L Ra-226), and the high level of radium in the raffinate suspended solids, it was concluded that radium had precipitated from solution and that a fresh sample of raffinate was necessary to complete the test. The other three liquids were deemed acceptable feedstock for use in the Key Lake waste treatment circuit simulation test.

A sample of fresh solvent extraction raffinate, requested from Key Lake Mining Corporation, was received at the SRC pilot plant on January 22, 1987. Analysis of this second raffinate sample is given in Table 3-2. From this analysis this fresh sample of raffinate was accepted for test purposes; hence the work scope for the addendum study was completed as outlined in Appendix A.

TABLE 3-1

ASSESSMENT OF ORIGINAL KEY LAKE WASTE SOLUTION SAMPLES

Sample	pH	Filtrate (0.45 micron)					Suspended Solids	
		Ra-226 (Bq/L)	Th-230 (Bq/L)	U (mg/L)	Fe (mg/L)	Pb (mg/L)	Weight (mg/L)	Ra-226 (Bq/g)
Minewater	3.8	25 ± 1.5	0.6 ± 0.03	0.6	0.23	0.04	9	8.0 ± 0.5
Raffinate	1.0	9.0 ± 0.5	55,000 ± 2,750	1.4	2,700	8.2	79	760 ± 45
Spent Regen. Sol'n	9.3	675 ± 40	190 ± 10	120	1.6	< 0.02	52	60 ± 4
Seepage and Supernatant	4.5	4.0 ± 0.2	0.35 ± 0.04	0.25	0.14	< 0.02	17	20 ± 1

TABLE 3-2
ANALYSIS OF FRESH RAFFINATE SAMPLE

Analyte	Filtrate (0.45 micron)	Suspended Solids
Ra-226	260 ± 21 Bq/L	500 ± 30 Bq/g
Th-230	40,000 ± 2,000 Bq/L	3,000 ± 150 Bq/g
U	0.8 mg/L	-
Ni	2,380 mg/L	-
As	2,200 mg/L	-
Fe	1,960 mg/L	-
Pb	14.4 mg/L	-
pH	1.1	-
Weight (mg/L)	-	50

4.0 RAFFINATE NEUTRALIZATION TESTS

4.1 METHODOLOGY

The batch-liming experiments carried out in the initial nickel arsenic study (August, 1986 Report) were repeated with the fresh raffinate sample.

A 20 L sample of fresh raffinate was neutralized with lime to pH 2 and the neutralized slurry was filtered through a No. 4 Whatman paper. A total of 18 L of filtrate was collected which implied that the pH 2 cake of 473.6 g (dry basis) contained 80% moisture upon vacuum filtration.

Separate batches of the collected pH 2 filtrate were then neutralized to increasing pH values, pH 3.5 to 11, and the resulting precipitate was collected by filtration, dried and submitted for analysis along with the collected filtrate.

4.2 RESULTS

The results of the batch-liming experiments are summarized in Table 4-1. The radium, thorium and uranium profiles of the filtrate solutions are depicted in Figures 4-1, 4-2 and 4-3. From these results it is evident that partial radium precipitation does occur, up to pH 7, without the presence of barium chloride. Thorium precipitation occurs in the acid pH range, being complete by pH 7. Uranium removal to trace levels is complete by pH 3.5. Iron removal occurs up to pH 7. Lead removal is complete by pH 2.

The decreasing radium, thorium and uranium concentrations in the solid precipitate with increasing pH of the solution is due to the increasing weight of precipitate produced at the higher pH values. The precipitate weight profile (dried at 110°C) is shown in Figure 4-4.

TABLE 4-1

RAFFINATE NEUTRALIZATION RESULTS

	pH 1*	pH 1-2	pH 2-3.5	pH 2-5	pH 2-6	pH 2-7	pH 2-11
FITRATE							
Ra-226(Bq/L)	260 ± 21	130 ± 10	95 ± 6	60 ± 4	20 ± 1.2	9 ± 0.5	8 ± 0.5
Th-230(Bq/L)	40,000 ± 2,000	2,000 ± 100	13 ± 1	3.0 ± 0.2	1.0 ± 0.5	0.08 ± 0.02	0.04 ± 0.02
U (mg/L)	0.8	0.27	0.02	0.002	0.011	0.031	0.006
Fe (mg/L)	1,960	1,510	1,590	1,490	1,200	1.02	0.05
Pb (mg/L)	14.4	0.1	0.1	< 0.05	< 0.05	< 0.05	< 0.05
Ni (mg/L)	2,380	2,250	2,060	-	-	-	-
As (mg/L)	2,200	1,680	420	-	-	-	-
$Ca(OH)_2$(g/L)	-	11.7	3.0	4.8	5.7	10.7	16.8
Volume (L)	-	18	1.47	1.45	1.47	1.35	1.42
PRECIPITATE							
Ra-226(Bq/g)	-	10 ± 0.6	7.5 ± 0.5	6 ± 0.4	6 ± 0.4	4 ± 0.3	3.5 ± 0.2
Th-230(Bq/g)	-	1,900 ± 95	30 ± 1.5	17 ± 1	8 ± 0.4	4.5 ± 0.2	3.5 ± 0.2
U (mg/kg)	-	26	30	18	18	7.4	6.3
Weight (g/L)	-	23.7	11.0	18.8	20.9	38.0	47.7

* solvent extraction raffinate feedstock

FIGURE 4-1
RAFFINATE NEUTRALIZATION TESTS
RADIUM-226 PROFILE

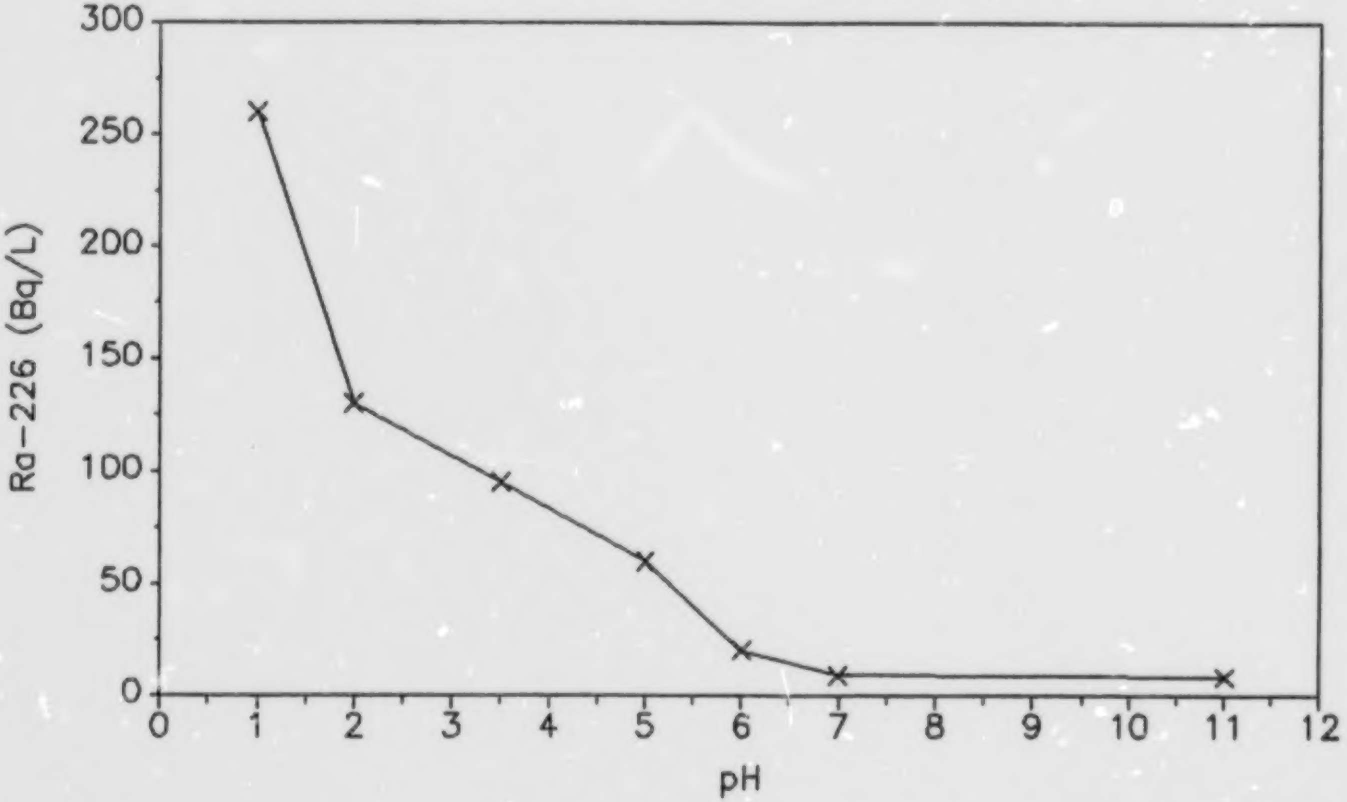


FIGURE 4-2
RAFFINATE NEUTRALIZATION TESTS
THORIUM-230 PROFILE

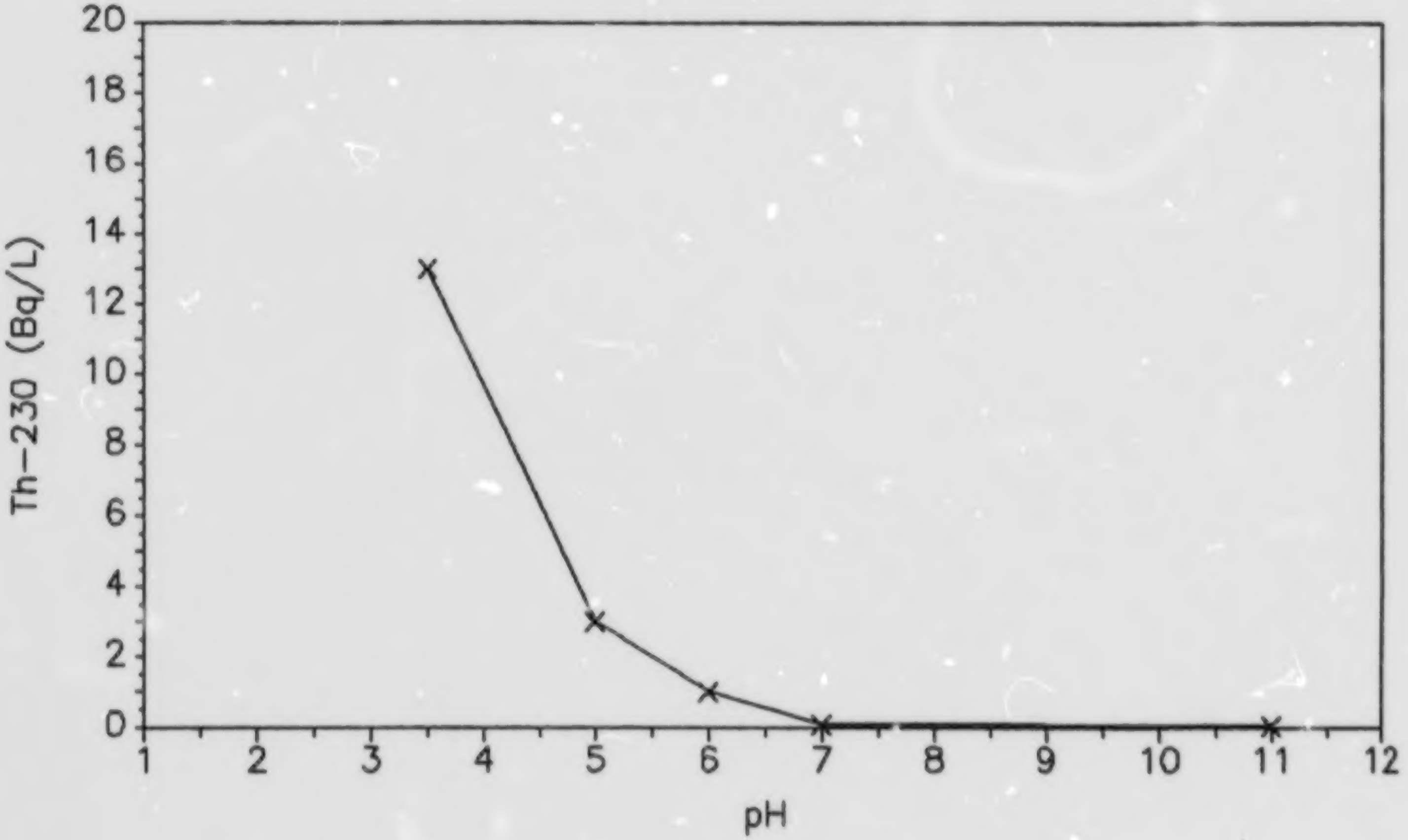


FIGURE 4-3

RAFFINATE NEUTRALIZATION TESTS
URANIUM PROFILE

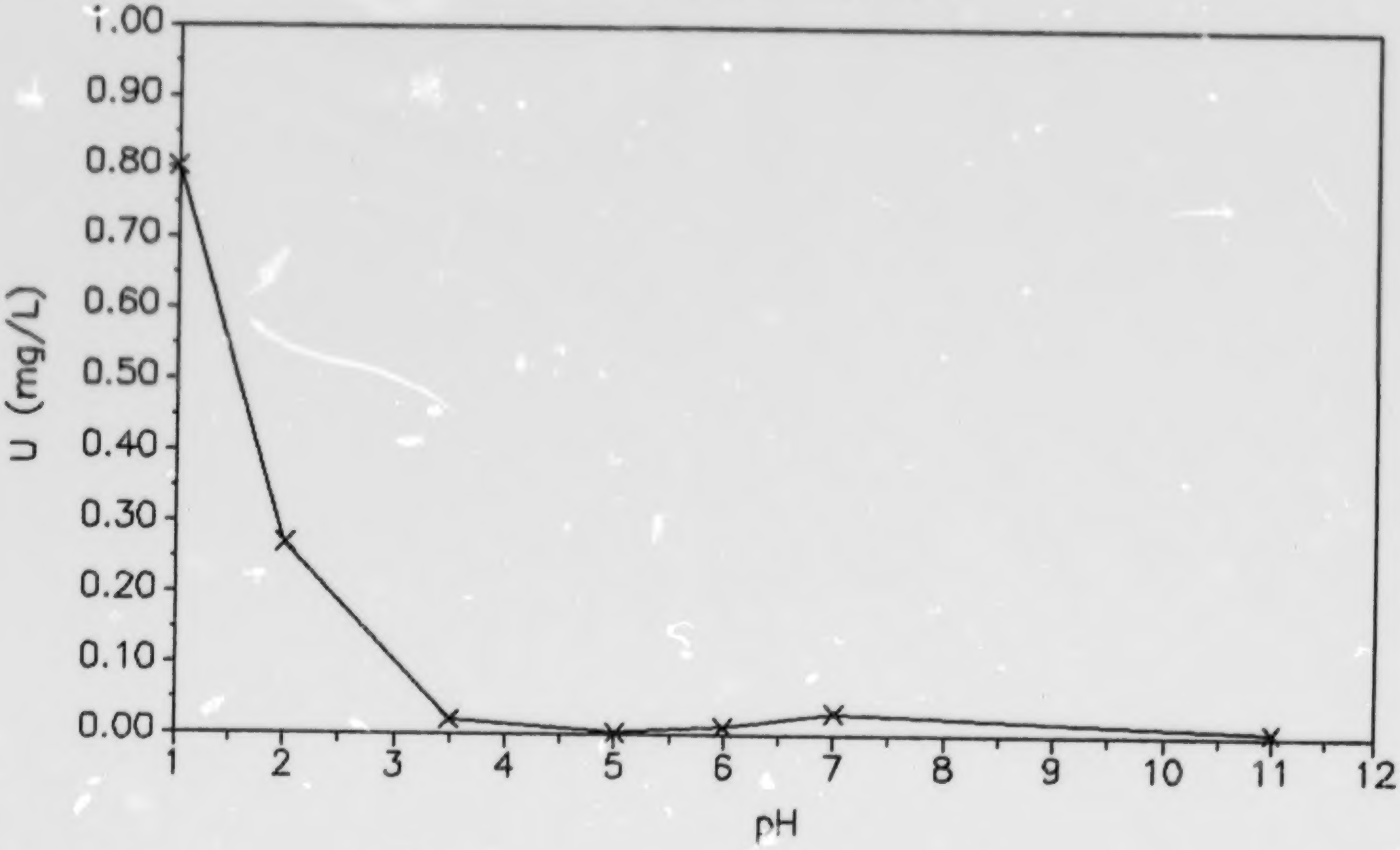
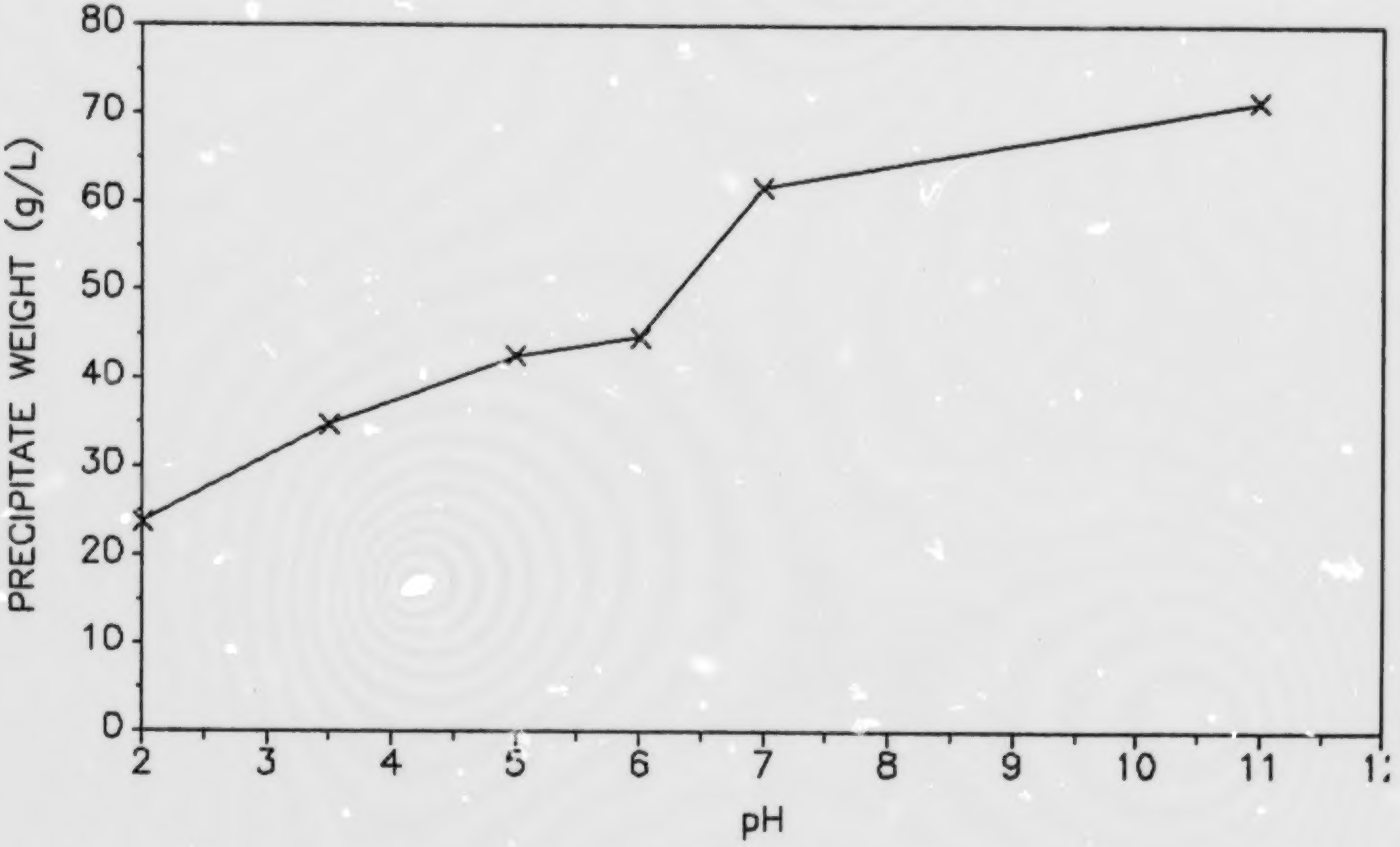


FIGURE 4-4
RAFFINATE NEUTRALIZATION TESTS
PRECIPITATE WEIGHT PROFILE



5.0 WASTE TREATMENT SIMULATION TEST

5.1 METHODOLOGY

A simulation of the Key Lake waste treatment circuit was carried out exactly as described in the August 1986 report by repeating the test procedure identified in Figure 5-6 of the earlier report. This test was done to produce a precipitate under laboratory conditions with the same characteristics as the waste precipitates produced in the Key Lake circuit.

The initial solution feed was 1.0 L of the fresh raffinate sample received from Key Lake and 0.013 L of spent regeneration solution used in the earlier test. The minewater and seepage and supernatant solution (available from the earlier work) were added in the same proportion as shown in Figure 5-6 of the earlier report, namely 0.42 L of minewater and 0.336 L of seepage and supernatant.

Lime was added as a 15% slurry in minewater, barium chloride was added as a 5% solution and flocculant (Percol E-24) was added as a 1 g/L solution prior to filtering the waste precipitates at pH 7 and pH 11. The pH 7 and pH 11 cakes were dried at 110°C and submitted for analysis along with the final filtrate solution.

5.2 RESULTS

The test conditions for the waste treatment simulation test are summarized in Table 5-1 and the test results are given in Table 5-2. Radium removal occurs in both stages of precipitation to provide a final filtrate assaying 0.40 Bq/L Ra-226 (diss.). Thorium removal is effected in the first stage treatment to give a final filtrate assaying 0.08 Bq/L Th-230 (diss.). Removal of trace uranium values is also completed in the first stage treatment to give a final filtrate assaying 0.025 mg/L U. It should be noted that the radium level in the treated effluent obtained at Key Lake, with appropriate recycle streams in the treatment circuit, is one order of magnitude lower than the value obtained in this single laboratory test.

TABLE 5-1

KEY LAKE WASTE TREATMENT SIMULATION TEST CONDITIONS

FIRST STAGE

Raffinate	1.0 L
Spent Regeneration Solution	0.013 L
Minewater	0.42 L
Seepage and Supernatant	0.336 L
pH	7
Lime slurry (15% S) added	141 mL
$Ca(OH)_2$ (100%) added	19.5 g
Filtrate recovered	1,698 mL
Precipitate recovered (dry weight)	49.34 g

SECOND STAGE

Barium chloride added (5% solution)	4 mL
pH	11
Lime slurry (15% S) added	27.5 mL
$Ca(OH)_2$ (100%) added	3.89 g
Filtrate recovered	1,660 mL
Precipitate recovered (dry weight)	6.91 g

TABLE 5-2

KEY LAKE WASTE TREATMENT SIMULATION TEST RESULTS

	Ra-226	Th-230	U
Final Filtrate	0.40 ± 0.04 Bq/L	0.08 ± 0.02 Bq/L	0.012 mg/L
pH 7 Precipitate	1.2 ± 0.1 Bq/g	750 ± 40 Bq/g	53 ppm
pH 11 Precipitate	27 ± 2 Bq/g	2.0 ± 0.1 Bq/g	3 ppm

6.0 PREPARATION AND EXAMINATION OF IRON ARSENATES

6.1 PREPARATION

Ferrous and ferric arsenate precipitates were prepared by the sodium hydroxide neutralization of arsenate solution containing 50 g/L sulphate ion and stoichiometric quantities of either ferrous or ferric sulphate. The precipitation reactions were carried out in a nitrogen atmosphere (glove box) and the products were dried at 30°C in a nitrogen-purged atmosphere.

The chemical reactions involved in the preparation of the ferrous and ferric arsenates were as follows:

Ferrous

$$2Na_2H\ AsO_4.7H_2O + 3\ FeSO_4.7H_2O \xrightarrow[NaOH]{H_2SO_4/Na_2SO_4} Fe_3(AsO_4)_2.xH_2O + 2Na_2SO_4 + H_2SO_4 + H_2O$$

Ferric

$$2Na_2H\ AsO_4.7H_2O + Fe_2(SO)_3.7H_2O \xrightarrow[NaOH]{H_2SO_4/Na_2SO_4} 2FeAsO_4.xH_2O + 2Na_2SO_4 + H_2SO_4 + H_2O$$

Ferrous Arsenate

The following reagent additions were followed in the preparation of ferrous arsenate:

- 6.525 g of secondary sodium arsenate in 750 mL of water with nitrogen bubbling in the water (pH 9.0)
- pH adjustment to 1.0 with sulphuric acid (11.29 g of SO_4 added)
- 38.774 g of sodium sulphate (to achieve 50 g/L SO_4) (pH 1.3)
- 8.72 g of $FeSO_4.7H_2O$ added (pH 1.3)
- neutralization to pH 5 with 178.36 g of 50 g/L NaOH solution
- precipitate was filtered and washed with 50 mL of buffered pH 5 water
- collected 44.627 g of wet precipitate which dried to a weight of 36.174 g at 30°C.

Ferric Arsenate

The following reagent additions were followed in the preparation of ferric asenate:

- 6.525 g of sodium arsenate in 750 mL of water with nitrogen bubbling in the water (pH 9.0)
- pH adjustment to 1.0 with sulphuric acid (9.11 g of SO_4 added)
- 42.005 g of sodium sulphate (to achieve 50 g/L SO_4) (pH 1.4)
- 5.635 g of $Fe_2(SO_4)_3.7H_2O$ added (pH 1.4)
- neutralization to pH 5 with 195.9 g of 50 g/L NaOH (pH 4.92)
- precipitate was filtered and washed with 50 mL of buffered pH 5 water
- collected 16.178 g of wet precipitate which dried to a weight of 15.129 g at 30°C.

The precipitates examined in the earlier work did not exhibit any crystalline structure, being identified as an amorphous mixture of hydrous oxides and hydroxides. Accelerated aging of the ferrous and ferric arsenate precipitates was therefore attempted by heating the two products in a nitrogen atmosphere at 110°C, 350°C and 500°C.

A weight loss comparison at increasing temperature is given in Table 6-1 for both ferrous arsenate and ferric arsenate. From the precipitate weight collected, and from the indicated weight loss upon heating, it is evident that ferrous arsenate precipitate contains a significantly higher level of water of hydration.

6.2 X-RAY DIFFRACTION ANALYSIS

The four ferrous arsenate precipitates and the four ferric arsenate precipitates were submitted for XRD analysis. The X-ray powder diffraction charts are shown in Figures 6-1 and 6-2. The sample reference numbers indicated on the charts are as follows:

Sample No.	Description
28	Ferric test at 30°C
29	Ferrous test at 30°C
30	Ferric test at 110°C
31	Ferrous test at 110°C
32	Ferric test at 350°C
33	Ferrous test at 350°C
34	Ferric test at 500°C
35	Ferrous test at 500°C

TABLE 6-1

IRON ARSENATES-WEIGHT LOSS COMPARISON (%)

	Ferrous Arsenate	Ferric Arsenate
30°C	18.9	6.5
110°C	91.1	43.0
350°C	88.8	65.9
500°C	89.4	65.1

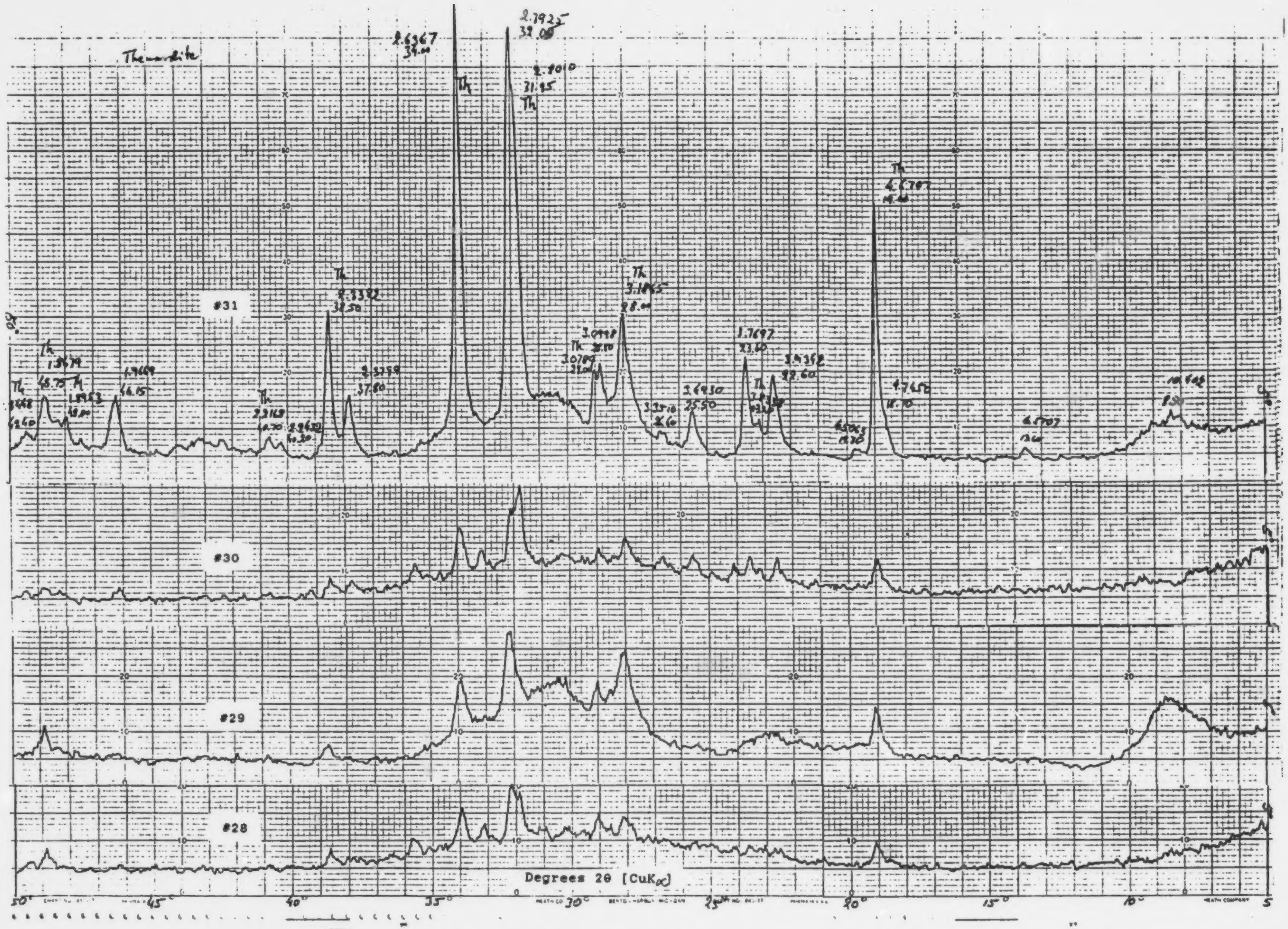


Figure 6-1 Iron Arsenate Precipitates-X-Ray Diffraction Patterns

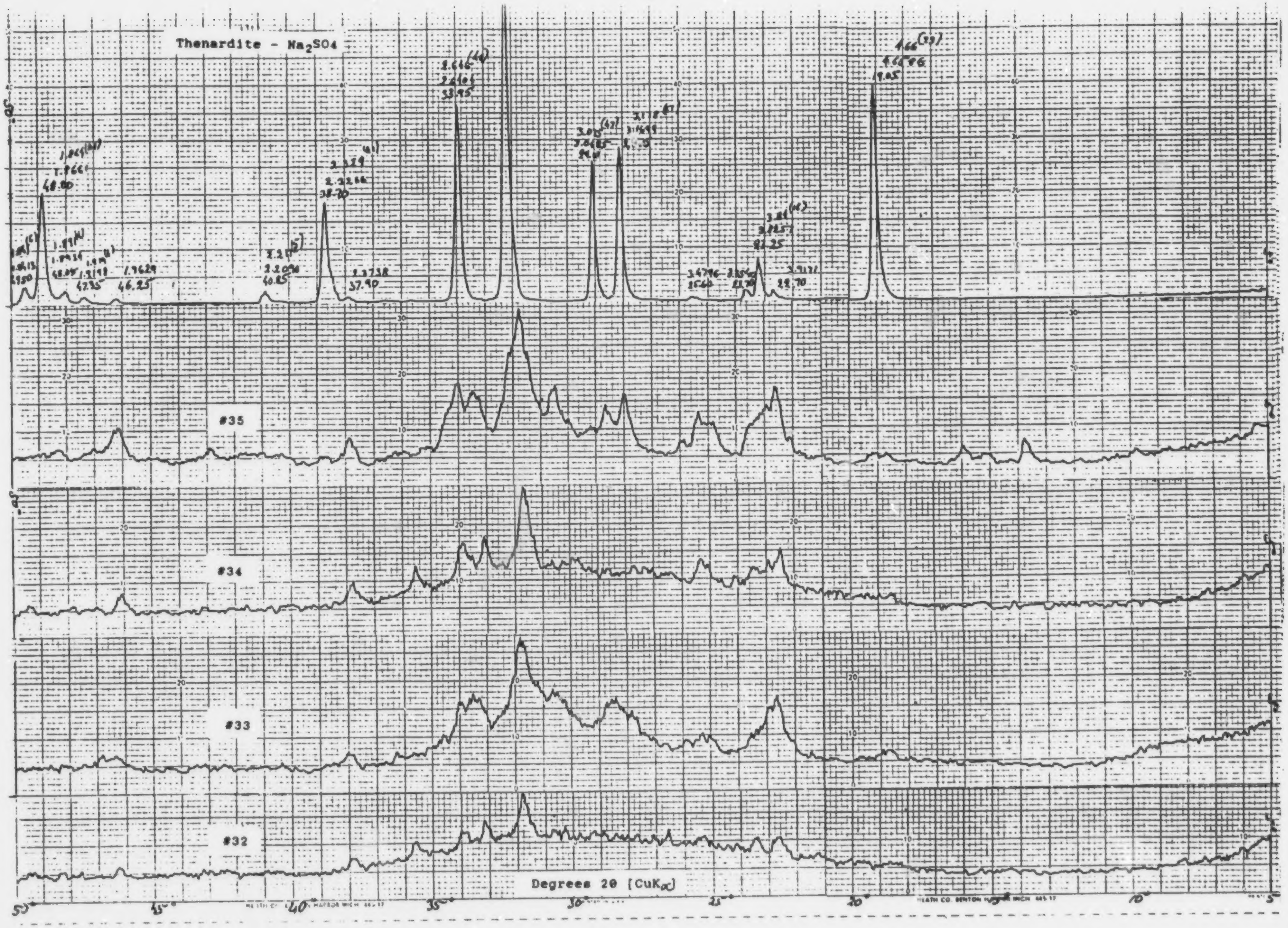


Figure 6-2 Iron Arsenate Precipitate-X-ray Diffraction Patterns

The charts indicate that the X-ray profiles for the precipitates are similar but that the quality of the profiles varies from sample to sample depending upon the degree of crystallinity and/or the quantity of the diffracting mineral. Only the profile of Sample No. 31 (the ferrous arsenate at 110°C) indicates a substantial quantity of a well developed crystalline mineral. The crystalline mineral in this sample was identified as Thenardite (sodium sulphate). An X-ray diffraction pattern of a pure sample of Thenardite is included in Figure 6-2 for comparison purposes. The other X-ray profiles appear to be Thenardite-like.

Thenardite is a white crystalline mineral and is probably the white material that can be observed in some of the samples. The greenish and brownish material, comprising a large proportion of some of the samples, was largely amorphous since these materials did not produce diffraction patterns.

A diffraction peak at about 30.5 degrees two-theta (d = 2.93 A) in some charts (Sample No. 35 for example), may indicate the presence of an arsenic sulfide (As_4S_3), but this could not be confirmed due to the interference of the other diffraction lines with those of Thenardite.

7.0 SYNTHETIC SOLUTION TEST

The synthetic solution test carried out in the earlier work to investigate the co-precipitation of arsenic with aluminum was repeated using ferrous and ferric sulphate in the place of aluminum.

A total of 17.472 g of $Na_2HAsO_4.7H_2O$ was added to 4 L of deionized water and the pH was adjusted to 1.9 with sulphuric acid (147.84 g).

To two separate 750 mL portions of this solution a total of 5.635 g of $Fe_2(SO_4)_3.7H_2O$ was added for the ferric test and 8.72 g of $FeSO_4.7H_2O$ was added for the ferrous test.

A total of 1.875 g of $CaSO_4.1/2H_2O$ was then added to each test and the solution allowed to mix overnight. Each gypsum-saturated solution was then filtered to remove any excess gypsum.

The ferric and ferrous solutions, saturated with gypsum, were then neutralized to pH 5 with lime, the resulting precipitate filtered from solution, and the filtrate analyzed for iron and arsenic. The precipitate weights recovered (dried at 110°C) were 7.43 g for the ferric test and 7.93 g for the ferrous test.

The filtrate from the ferric test assayed 0.85 g/L Fe and 0.24 g/L As while the filtrate from the ferrous test assayed 0.047 g/L Fe and 0.069 g/L As. The lower arsenic assay obtained in the ferrous test is an indication that ferrous iron is definitely associated with the precipitation of arsenic from solution.

8.0 IRON AND ARSENIC SPECIATION ANALYSIS

The earlier work had indicated the presence of a subtantial amount of arsenite ion in Key Lake solvent extraction raffinate. To confirm the presence of arsenite ion in Key Lake raffinate additional fresh samples of Key Lake raffinate were analyzed for arsenic, arsenic(III) and arsenic(V) as well as iron, iron(II) and iron(III). Total arsenic analysis was by X-ray and DCP and As(III) and As(V) were analyzed by AA-vapor generation. Total iron analysis was by DCP, titrimetry and X-ray. The Fe(II) and Fe(III) analysis were by titrimetry. The analytical results are presented in Table 8-1.

These assays indicate that the arsenate to arsenite ratio ranged from 1.7/1 to 2.6/1 and the ferric to ferrous ratio averaged 1/7. The high proportion of ferrous iron to ferric iron suggests that ferrous arsenate is likely an important component in the precipitation of arsenic from Key Lake raffinate. This fact is consistent with the results of the synthetic test described in the previous section.

TABLE 8-1

IRON AND ARSENIC SPECIATION ANALYSIS (g/L)
KEY LAKE SOLVENT EXTRACTION RAFFINATE

	Arsenic			Ratio	Iron			Ratio
Raffinate	**Total**	**As^{3+}**	**As^{5+}**	**As^{5+}/As^{3+}**	**Total**	**Fe^{2+}**	**Fe^{3+}**	**Fe^{2+}/Fe^{3+}**
26/1/87	3.25	1.20	2.05	1.7/1	2.79	2.46	0.33	7.5/1
29/1/87	3.32	0.93	2.39	2.6/1	2.71	2.33	0.38	6.1/1
30/1/87	3.02	1.09	1.93	1.8/1	2.78	2.45	0.33	7.4/1
Average	3.20	1.07	2.12	2.0/1	2.76	2.41	0.35	6.9/1

9.0 ANALYTICAL METHODOLOGY

9.1 QUALITY CONTROL

The SRC Analytical Laboratory participates in more than ten inter-laboratory quality assurance programs within Canada and the United States. Most of these programs are repeated two to four times annually. The programs encompass trace metal measurements on water and solids, major water constituents and radiochemical determinations on liquids, solids and filters. All methodology is checked for recovery, precision and accuracy by analyzing NBS, CANMET and similar reference standards. The laboratory has routinely participated in the standardization of reference materials, primarily in the radiochemical field.

In addition blind duplicates, spiked samples and blanks are routinely processed with each group of samples analyzed. These internal quality control checks constitute approximately 10% of the analytical workload. All radiochemical procedures are calibrated and checked with NBS traceable standards, some directly from NBS and others from Amersham.

9.2 RADIOCHEMICAL ANALYSIS

Radium-226

Sample decomposition: Potassium pyrosulphate fusion

In this procedure, radium is isolated by first being precipitated with lead sulphate and then selectively precipitated with barium sulphate. The radium in the precipitate is determined either by alpha spectroscopy, or by gross alpha counting if thorium is known to be absent.

Reference Standard:

Amersham RAY.44 Soln.#R1/300/54

Overall uncertainty $^{+}$ 3.7%

Thorium-230

Tracer: Thorium-234

Sample decomposition: Potassium pyrosulphate fusion

Thorium is separated from prepared sample solutions by coprecipitation with barium sulphate. Barium sulphate is dissolved in a strongly alkaline solution of ethylenediaminetetraacidic acid. Thorium is precipitated as hydroxide with 50 micron cerium carrier. The precipitate is mounted on a 25 mm 0.2 micron membrane filter for alpha spectrometry. Alpha spectrometry is performed using a vacuum chamber mounted surface barrier detector.

Reference Standard:

Std#1 Amersham aged thorium nitrate

Std#2 Alfa Chemicals thorium oxide 99.9%

It is assumed that Th-230 would give the same response as Th-232 and Th-228 from these standards (ie. cpm/pCi).

APPENDIX A

ORIGINAL STATEMENT OF WORK

RECEIVED
OCT 23 1986
MELIS CONSULTING
ENGINEERS LTD.

APPENDIX I

STATEMENT OF WORK

Amendment to DSS Contract Serial No. 23317-6-1727/01-SQ

The following additional objectives are required, to be reported in a separately bound addendum to the final report "Study of the State of Nickel and Arsenic in Uranium Mill Tailings" by Melis Consulting Engineers Limited.

Addendum I: Measurements of the disposition of uranium, radium-226 and thorium-230 upon raffinate liming.

1.1 Establish condition of stored mine waste stream solutions.

The four Key Lake waste stream solution samples, i.e. the solvent extraction raffinate (Code SXR), mine water (MW), seepage/supermate (SEP) and spent regeneration solution (RS) will be examined for evidence of precipitation since their acquisition. The pH of each solution will be measured, and should this have changed due to storage, be readjusted to the sampling value, and each solution then should be stirred for re-equilibration.

Residual solids will be separated by filtration, dried, weighed and submitted for determination of concentrations of radium-226, uranium and thorium-230.

The four filtrates SXR, MW, SEP and RS will be sampled and the samples submitted for determinations of concentrations of radium-226, thorium-230 and uranium. Each result should include an analytical uncertainty estimate. Each filtrate will additionally be analysed for total iron and lead concentrations.

1.2 Should an appreciable fraction of the radium-226 of sample SXR be associated with the precipitate from this sample, the Scientific Authority will be informed and a decision to proceed or not to proceed with subsequent work in this Addendum will be made in consultation with the Scientific Authority. Costs associated with work for Addendum I will be appropriately reduced should work cease at this point.

1.3 Thorium-230, radium-226 and uranium disposition in raffinate batch-liming experiments.

Batch-liming experiments of raffinate from pH 1 to pH 2; and of filtrate from the pH 2 liming to: pH 3.5, pH 5, pH 6, pH 7, and pH 11 respectively will be carried out in an analogous manner to that described in Section 5.3.2 of the final report draft "Study of the State of Nickel and Arsenic in Uranium Mill Tailings". This will yield six filtrate (solution) and six precipitated products. The concentrations of uranium, thorium-230 and radium-226 will be determined for each of the six precipitate products. Each value should be accompanied by an analytical uncertainty estimate. Additionally, the six filtrate solutions will be analysed for iron and lead concentrations. The pH 3.5 sample will, in addition, be analysed for Ni and arsenic concentrations. Solids should be dried at 110° prior to measurement. Volume, weight, and pH inventories will be reported for each experiment.

NOTE: The above series of experiments differ from the series employed for the nickel and arsenic balance in that a final pH 3.5 experiment is added and final pH experiments of 8 and 9 have been dropped.

1.4 Thorium-230, radium-226 and uranium disposition in Key Lake waste treatment simulation test.

The waste treatment simulation test as described in Section 5.3.2 and Figures 5-6 of the final report draft "Study of the State of Nickel and Arsenic in Uranium Mill Tailings" will be repeated. This will yield three products: a filter cake obtained following neutralization to pH 7; a filter cake following neutralization to pH 11, and a final filtrate. These products will be analysed for thorium-230, radium-226, and uranium. Analytical uncertainty estimates should be reported with each value. Precipitates should be dried at 110°C. The volume/weight inventory for the experiment will be reported.

1.5 The addendum to the report will tabulate the results of the above experiments, briefly describe the methodology with reference to the main body of the report (noting any changes), and document the analytical and radiochemical methodology applied (including the quality assurance protocol of the laboratory used for this work, and the calibration reference materials employed for radium-226 and thorium-230 measurements, and comment on any implications of analytical uncertainties.

Addendum II: Properties of ferrous and ferric arsenates.

2.1 Synthetic formulation of ferrous and ferric arsenates.

2.1.1 Preparation of reference ferrous and ferric arsenates.

Ferrous and ferric arsenate compounds will be prepared by sodium hydroxide neutralization to pH 5 of arsenate solution at pH 1 containing 50g/L sulphate ion (sodium sulphate) to which stoichiometric quantities of ferrous and ferric sulphate have been added. These will be filtered and washed with water at pH 5. The ferrous arsenate preparation will be carried out in a nitrogen purged atmosphere. The compounds will be dried at 30°C in an N_2 atmosphere or vaccum atmosphere.

2.1.2 Feasibility of identification of ferrous and ferric arsenates by Xray diffraction.

The ferrous and ferric arsenates of 2.1.1 will be examined by XRD. The samples will be heated to 110°C in a vacuum or nitrogen atmosphere, and re-examined by XRD. The heat treatment and re-measurement will be repeated at 350°C and 500°C (eight XRD examinations).

2.1.3 The analogous experiments to the synthetic solution test as described in Section 5.3.2 of the final report draft "Study of the State of Nickel and Arsenic in Uranium Mill Tailings" will be carried out with ferrous and ferric sulphates replacing aluminum. Concentrations of iron and arsenic in the filtrates will be measured.

2.2 The contractor will endeavour to obtain and report quantitative information on the ratios As(III)/As(V), As/Fe and Fe(II)/Fe(III) present in Key Lake barren raffinates prior to waste treatment.

2.3 The Addendum report will describe the methodology and experimental results of 2.1 and 2.2, relate this information to the studies and conclusions contained in the main body of the report.

NATIONAL URANIUM TAILINGS PROGRAM

Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

Canada

STUDY OF THE STATE OF
NICKEL AND ARSENIC
IN URANIUM MILL TAILINGS

MCEL Project No. 115
FINAL REPORT
August, 1986

DSS File No. 15SQ.23317-6-1727
Contract No. 23317-6-1727/01-SQ

prepared for

DEPARTMENT OF ENERGY, MINES AND RESOURCES
CANADA CENTRE FOR MINERAL AND ENERGY & TECHNOLOGY
NATIONAL URANIUM TAILINGS PROGRAM

by

MELIS CONSULTING ENGINEERS LTD.
in association with
SASKATCHEWAN RESEARCH COUNCIL
and
SENES CONSULTANTS LIMITED

137 pp

MICROMEDIA

MELIS CONSULTING ENGINEERS LTD.
Metallurgical Engineering Services
519 45th Street West
Saskatoon, Saskatchewan, Canada
S7L 5Z9
(306) 652-4084
Telex: 074-2683 (NORPLEX)

September 17, 1986

Department of Energy, Mines and Resources
CANMET
National Uranium Tailings Program
555 Booth Street
Ottawa, Ontario
K1A 0G1

Project No.: MCEL-115
DSS Contract No.: 23317-6-1727/01-SQ

Attention: Dr. C. Smith

Dear Dr. Smith:

We are pleased to submit twenty-five copies of the Final Report entitled "Study of the State of Nickel and Arsenic in Uranium Mill Tailings". This work has been completed for the National Uranium Tailings Program by Melis Consulting Engineers Ltd. in association with the Saskatchewan Research Council and SENES Consultants Limited.

We trust the results of the study prove useful to the National Uranium Tailings Program and we appreciate the opportunity of being of service to the Department of Energy, Mines and Resources on this project. We remain available to discuss any aspect of the report at your convenience.

Respectfully submitted,

MELIS CONSULTING ENGINEERS LTD.

L.A. Melis

L.A. Melis, P.Eng.

LAM/dcs

Enclosures

STUDY OF THE STATE OF
NICKEL AND ARSENIC
IN URANIUM MILL TAILINGS

TABLE OF CONTENTS

Page No.

1.0 SUMMARY 1-1

2.0 INTRODUCTION 2-1

3.0 KEY LAKE PROCESS DESCRIPTION 3-1
  3.1 Ore Characteristics 3-1
  3.2 Mill Circuit Description 3-3

4.0 NICKEL AND ARSENIC BALANCE 4-1
  4.1 Details 4-1
  4.2 Summary 4-5

5.0 LABORATORY TESTWORK 5-1
  5.1 General 5-1
  5.2 Sample Description 5-2
  5.3 Test Methodology and Results 5-4
  5.4 Quality Assurance 5-28

6.0 MINERALOGICAL EXAMINATION OF PRECIPITATES 6-1
  6.1 General 6-1
  6.2 Physical Characterization 6-3
  6.3 Chemical Characterization 6-5

7.0 GEOCHEMICAL MODEL 7-1
  7.1 General 7-1
  7.2 Basic Principles and Data 7-4
  7.3 Solid/Liquid Analysis 7-8
  7.4 Geochemical Model for Arsenic Precipitation 7-16
  7.5 Geochemical Model for Nickel 7-31

TABLE OF CONTENTS (Continued)

8.0 CONCLUSIONS AND RECOMMENDATIONS 8-1

9.0 REFERENCES 9-1

APPENDIX A Original Statement of Work

APPENDIX B Mineralogy Report

APPENDIX C Preparation of Raman Spectroscopy Reference Standards

STUDY OF THE STATE OF NICKEL AND ARSENIC IN URANIUM MILL TAILINGS

LIST OF TABLES

Table No.	Description	Page No.
3-1	Typical Analysis of Key Lake Ore	3-2
3-2	Key Lake Leach Circuit Conditions	3-4
4-1	Basis of Nickel and Arsenic Balance	4-3
5-1	Key Lake Solution Analyses	5-3
5-2	Gypsum Precipitation Conditions	5-6
5-3	Gypsum Precipitation Analyses	5-7
5-4	Raffinate Precipitation Conditions - pH Variation	5-9
5-5	Raffinate Precipitation Results - pH Variation - Filtrate Analyses	5-10
5-6	Raffinate Precipitation Results - pH Variation - Precipitate Analyses	5-11
5-7	Raffinate Precipitation Results - pH Variation - Ni/As Distributions	5-12
5-8	Raffinate Precipitation Results - pH Variation - Cumulative Removal Efficiencies of Major Elements	5-13
5-9	Raffinate Precipitate Conditions - Reaction Time Variation	5-20
5-10	Raffinate Precipitation Results - Reaction Time Variation - Filtrate and Precipitation Analyses	5-21
5-11	Raffinate Precipitation Results - Reaction Time Variation - Ni/As Distributions	5-22
5-12	Key Lake Simulation Test Results	5-25
6-1	List of Precipitates for Mineralogical Examination	6-2
6-2	Analysis of Precipitate Residues	6-6
6-3	Reference Standards for Raman Microprobe Analysis	6-8
7-1	Solubility and Complexation Equilibria	7-5
7-2	Ionic Strength and Activity Coefficients vs pH for Limed Raffinate	7-7

LIST OF TABLES (Continued)

7-3 Molar Concentration of Limed Raffinate Precipitates at Various pH Values 7-9

7-4 Molar Concentration of Soluble Constituents in Limed Raffinate 7-15

7-5 Predicted Arsenic Concentrations for $AlAsO_4$ Precipitation 7-21

7-6 Predicted Arsenic Concentrations for $Fe_3(AsO_4)_2$ Precipitation 7-27

7-7 Nickel Hydroxide Model Predictions 7-33

7-8 Nickel Hydroxide-Sulphate Model Predictions 7-35

STUDY OF THE STATE OF
NICKEL AND ARSENIC
IN URANIUM MILL TAILINGS

LIST OF FIGURES

Figure No.	Description	Page No.
4-1	Nickel/Arsenic Metallurgical Balance - Key Lake Milling Circuit	4-2
4-2	Nickel/Arsenic Balance Summary	4-6
5-1	pH Variation Tests - Precipitate Produced vs pH	5-14
5-2	pH Variation Tests - As, Al, PO_4 Removal Efficiencies	5-15
5-3	pH Variation Tests - Ni, Mg, Fe Removal Efficiencies	5-16
5-4	pH Variation Tests - Zn, SiO_2, SO_4 Removal Efficiencies	5-17
5-5	Reaction Time Variation - Nickel-Arsenic Removal	5-23
5-6	Key Lake Waste Treatment Simulation Test	5-24
7-1	Limed Raffinate Quality - As, Ni, Fe, SO_4, Cu	7-12
7-2	Limed Raffinate Quality - As, Ni, Si, Zn, Mg	7-13
7-3	Limed Raffinate Quality - As, Ni, Al, PO_4, Ca	7-14
7-4	Geochemical Model for Arsenic	7-30
7-5	Geochemical Model for Nickel	7-36

ACKNOWLEDGEMENTS

The full cooperation of Key Lake Mining Corporation in this study was greatly appreciated and is hereby acknowledged. Support from senior management at Key Lake and technical assistance from the metallurgical staff contributed significantly to the completion of the work detailed in this report.

STUDY OF THE STATE OF NICKEL AND ARSENIC IN URANIUM MILL TAILINGS

1.0 SUMMARY

The National Uranium Tailings Program office of the Department of Energy, Mines and Resources commissioned Melis Consulting Engineers Ltd. to perform a study on the state of nickel and arsenic in uranium mill tailings. This work was carried out in association with the Saskatchewan Research Council and SENES Consultants Limited between May and August, 1986.

The study was based on uranium tailings from the Key Lake mining operation in northern Saskatchewan. Waste solutions from the Key Lake milling circuit were used to produce waste precipitates for evaluation and to provide chemical data for the neutralization reactions. Several precipitates were examined mineralogically in an attempt to determine the chemical and physical nature of the nickel and arsenic in the waste precipitates.

A detailed nickel/arsenic metallurgical balance for the Key Lake circuit indicated that approximately 55% of the nickel and 60% of the arsenic in the Key Lake tailings are present in the form of chemical precipitates produced in the waste treatment circuit. Mineralogical examinations of these precipitates were not successful in identifying the nature of these precipitates since no crystalline nickel or arsenic precipitates could be determined. The precipitates appeared to be a mixture of amorphous solids of hydrous oxides and hydroxides.

Geochemical modelling of the test results cannot be considered conclusive since the exact chemical nature of the precipitates could not be identified. Consequently, the long-term implications for predicting tailings porewater quality remain somewhat conjectual.

Implications are that aging does not have a detrimental effect with regard to the dissolution of arsenate precipitates. In the anoxic environment of tailings porewater, iron(II) arsenates are thermodynamically stable whereas

the dissolution rates of iron(III) and aluminum arsenates are probably sufficiently low to allow readsorption of dissolved arsenate on metal hydroxide surfaces. In addition, dissolved iron(III) may be reduced to iron(II), during oxidation of arsenic(III) to arsenic(V), thereby allowing the reprecipitation of iron(III) arsenate as iron(II) arsenate. The combined effect of these mechanisms would yield arsenate concentrations in the mg/L range.

A geochemical model which describes the measured data for nickel has been developed. The model assumes that nickel hydroxide is the predominant species under alkaline conditions, above pH 8, and that a nickel hydroxysulphate complex controls solubility below this level. There is strong evidence that nickel precipitates become more stable as they are aged.

Long-term nickel levels in uranium tailings porewater will be a function of seepage, pH and sulphate levels. With the elevated gypsum content of the tailings, sulphate levels are expected to be elevated for thousands of years. Therefore nickel concentrations in seepage would be expected to fall into the 0.5 to 5 mg/L range for the stable nickel hydroxysulphate complex in a pH range of 6-7.

Further detailed laboratory investigations are required to better understand the solution chemistry and to chemically identify the exact nature of the nickel and arsenic precipitates. Additional work should also be done to verify iron and arsenic speciation in the Key Lake milling and waste treatment circuits. Monitoring of Key Lake tailings porewater and seepage should be continued to verify and improve upon the tentative geochemical models that have been put forward for arsenic and nickel.

STUDY OF THE STATE OF NICKEL AND ARSENIC IN URANIUM MILL TAILINGS

2.0 INTRODUCTION

The National Uranium Tailings Program (NUTP) was established by the Department of Energy, Mines and Resources to address the long-term environmental concern of mill tailings from uranium mining operations. Although radionuclides are the major contaminant concern of uranium mill tailings there is a need to address other non-radionuclide components of tailings in light of their potential long-term impact on the environment.

Tailings from some of the currently operating Saskatchewan uranium mines (Key Lake and Collins Bay B-Zone) and the orebodies of future operations (Cigar Lake) contain appreciable quantities of nickel and arsenic. Previous studies were commissioned by the NUTP office to investigate these two components in terms of their mode of occurrence in the tailings and in regard to the potential for re-dissolution and migration of these two elements from tailings containment areas (Knight and Piesold Ltd., 1985, 1986; Beak Consultants Limited, 1986). These studies identified that the nature of nickel and arsenic in uranium tailings was not clearly defined and that a study should be carried out to attempt to determine the chemical and physical make-up of these two elements in uranium tailings.

Melis Consulting Engineers Ltd. (MCEL) was commissioned by the NUTP office to carry out this study under contract to the Department of Supply and Services. The study was based on the Key Lake uranium mining operation in northern Saskatchewan since Key Lake tailings had been used in a previous NUTP study (Knight and Piesold Ltd., 1985).

The original statement of work for the study is provided in Appendix A. The main objectives of the study were to identify the dissolution behaviour of nickel and arsenic minerals in the Key Lake milling circuit and to investigate the nature of nickel and arsenic complexes in uranium mill tailings. This was to be accomplished by calculating nickel and arsenic metallurgical balances in the Key Lake milling circuit and by producing chemical precipitates from Key Lake mill waste solutions in order to determine their chemical and physical composition. The experimental data generated was then used in chemical equilibrium modelling studies to develop and assess precipitation-dissolution mechanisms for nickel and arsenic in uranium mill tailings.

Melis Consulting Engineers Ltd. was assisted in the study by Key Lake Mining Corporation who provided appropriate samples of mill solutions as well as other pertinent information required for the study. The testwork was carried out at the Saskatchewan Research Council (SRC) facilities in Saskatoon, Saskatchewan under the direction of MCEL. SRC was also responsible for chemical analysis of solutions and precipitates and for mineralogical examinations of the precipitates produced in the testwork. SENES Consultants Limited were retained to perform the geochemical modelling studies to assess and predict the precipitation-dissolution mechanisms for nickel and arsenic in uranium mill tailings.

3.0 KEY LAKE MILLING CIRCUIT

3.1 ORE CHARACTERISTICS

The Key Lake mine, operated by Key Lake Mining Corporation of Saskatoon, Saskatchewan, is located approximately 240 km north of LaRonge, Saskatchewan, 70 km east-southeast of Cree Lake. The Key Lake uranium deposit consists of two separate orebodies, the Gaertner orebody and the Deilmann orebody. Both orebodies contain uranium mineralization associated with nickel arsenides.

The uranium ore minerals include euhedral and radially textured pitchblende [U_3O_8], and smaller amounts of coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$]. Gersdorffite [(Ni,Co)AsS] is the most abundant nickel mineral followed by niccolite [NiAs] and bravoite [$(Ni,Fe)S_2$]. Galena [PbS] of radiogenic origin is always present. Within the unaltered basement rocks, pyrrhotite [$Fe_{1-x}S$] and chalcopyrite [$CuFeS_2$] have been observed. Extensive intergrowth of uranium and nickel minerals is present. Sooty pitchblende and coffinite can constitute the matrix for gersdorffite, millerite, niccolite and galena or vice versa.

Above the ore-bearing basement uranium-nickel mineralization occurs intermittently disseminated in porous and fractured sandstone and conglomerate. Chlorite schist is the main uranium-nickel bearing host rock with quartzite host having a distinctly lower grade. In both the chlorite and quartzite hosts limonite [$FeO(OH).nH_2O$], hematite [Fe_2O_3] and carbonates [CO_3] can accumulate in shear zones, cavities and fractures. Graphite [C] is present throughout the mineralization.

Typical analyses of the Gaertner and Deilmann ore at Key Lake are listed in Table 3-1. The nickel and arsenic content given for the Gaertner ore is the average ore grade of the mill feed for the operating period January, 1985 to April, 1986. The other analyses given are average values reported in a previous publication (Clarke et al., 1980).

TABLE 3-1

TYPICAL ANALYSIS OF KEY LAKE ORE (%)

Element	Gaertner Ore	Deilmann Ore
U_3O_8	2	2.9
Ra-226	222 Bq/g	N/A
SiO_2	50	50
Fe	3.5	3
S	1	0.8
Cu	0.03	0.09
Zn	0.08	0.03
Mo	0.006	0.03
V	0.08	0.09
Ni	1.9	1.1
Co	0.08	0.08
Ti	0.4	0.6
Al	9	10.3
As	1.2	1.1
Ca	0.4	0.4
Mg	3	2.9
Na	0.7	0.9
K	0.6	1.5
F	0.05	N/A
P_2O_5	0.16	0.15
CO_2	1	0.8
Cl	0.05	N/A

3.2 MILL CIRCUIT DESCRIPTION

The leaching process for nickel-arsenic uranium ores is not significantly different from other uranium acid leaching circuits although relatively high acid concentrations must be maintained to ensure high uranium extraction and to stabilize the leach liquor for preventing reprecipitation of uranium with other ions in solution. High oxidant addition is required in order to ensure sufficient oxidant for oxidizing all of the uranium to the hexavalent state in the presence of non-radionuclide contaminants in the ore.

At Key Lake the ore is ground in a SAG (semi-autogenous grinding) mill to a mesh-of-grind of minus 500 micron. The ground ore is dewatered in a thickener to a pulp density of 50% solids with the addition of a flocculant to assist in settling. The thickened pulp is then pumped to a two-stage leaching circuit where the ore is leached with sulphuric acid under oxidizing conditions. Typical leaching conditions for the two stages are given in Table 3-2. A two-stage circuit is used in order to recycle acid solutions for reducing overall acid consumptions and to prevent formation of ferric arsenate in the pregnant solution by providing reducing conditions, namely fresh ore feed, for the ferric iron contained in the recycled acid solution.

The ground ore is fed from storage pachucas at a nominal rate of 30 tonnes/hour to first-stage air-agitated pachucas where it is contacted with reclaimed acid solution (thickener overflow solution) from the second-stage leach and leached at atmospheric pressure and relatively low pulp density and temperature. Oxidant requirements in the first-stage leach are met by the injection of air used for agitation in the pachucas. The ferric content in the thickener overflow solution also acts as an oxidant for the leaching reactions. Acid requirements for the first-stage leach are met by the elevated acid level of the thickener overflow solution and by the addition of additional sulphuric acid as required.

The first-stage leach pulp is then pumped to the primary thickener where the thickener underflow is removed at 50% solids and pumped to the second-stage pressure leach feed tank. The overflow from the primary thickener is the pregnant solution which is pumped to solution pre-treatment ahead of the solvent extraction circuit.

TABLE 3-2
KEY LAKE LEACH CIRCUIT CONDITIONS

	First Stage	Second Stage
Particle Size (% - 74 microns)	50	50
Pressure (kPa)	atmospheric	600
Temperature (°C)	25-30	60
Acid Concentration (g/L H_2SO_4)	>12	>40
Acid Consumption (kg/t H_2SO_4)	40	90
Pulp Density (% solids)	15-20	50
Retention time (h)	1	4

Second-stage pressure leaching of the pre-leached ore slurry is carried out in a series of nine vertical pressure autoclaves. Sulphuric acid is added to the autoclave feed tank to provide the necessary acid levels for achieving high uranium extractions. Oxidant requirement is met by the injection of oxygen in the autoclaves. The second-stage leach slurry is then discharged into a surge tank for transfer to the eight-stage counter-current-decantation (CCD) circuit.

The overflow from the first-stage thickener in the CCD circuit is the acid solution recycled to the first-stage leaching step. Additional sulphuric acid is added in the CCD circuit in order to maintain adequate acid levels for preventing loss of uranium by reprecipitation. Minewater is used as wash water to effectively wash uranium-containing solution from the leached ore. The underflow from the last CCD thickener is pumped to the tailings neutralization circuit.

Uranium in the pregnant solution from the CCD circuit is upgraded and purified in a solvent extraction circuit utilizing a tertiary amine organic phase and ammonia stripping of loaded organic. The pregnant strip liquor is precipitated with ammonia to produce yellowcake and the barren strip solution from the precipitation circuit is recycled to the solvent extraction. Ammonium sulphate concentrations in the strip liquor are controlled by removing a bleed stream of clarified strip solution to an ammonium sulphate crystallization circuit. The ammonium sulphate crystals are produced as fertilizer-grade material and marketed as 21-0-0 fertilizer. Spent organic is regenerated with sodium carbonate solution as required.

The leach residue from the CCD circuit is neutralized with lime to pH 11 or greater and liquid waste streams are neutralized and treated in a separate waste treatment circuit.

In the liquid waste treatment circuit (referred to as the Bulk Neutralization circuit) raffinate and minor quantities of spent sodium carbonate solution from the solvent extraction circuit are first neutralized in a stepwise fashion with lime to pH 7. Seepage and supernatant recycled from the tailings pond, along with excess minewater, are combined with the resulting precipitate slurry and the dilute slurry is thickened to recover a bulk waste precipitate which is discharged to the mill tailings neutralization circuit. The thickener overflow is further treated with barium chloride and lime to pH 11 to remove radium and trace heavy metal contaminants. The minor amounts of additional precipitate produced in this second-stage treatment are removed in a thickener and pumped to the mill tailings neutralization circuit. The pH of the second-stage thickener overflow is adjusted with sulphuric acid and the treated effluent is transferred to monitoring ponds. The effluent is either discharged to the environment, if contaminant levels are acceptable, or recycled for further treatment if necessary.

Minewater from the open-pit mining operation is used as process water and any excess contaminated water is treated in the waste treatment circuit. An ion exchange circuit has also been used to treat excess tailings water. In this circuit radium is removed by a radium-selective ion exchange complexer and the treated water is discharged to the monitoring ponds.

The combined neutralized mill tailings, consisting of neutralized leach residue and waste precipitates, are pumped to the tailings containment area where a layered tailings deposition technique is utilized. With this method of tailings placement, the tailings slurry is deposited in thin layers in a rotational sequence and allowed to consolidate by evaporation and drainage. This systematic layered deposition method is claimed to provide a partially saturated, moisture retaining tailings mass of low permeability, with minimum potential for ongoing seepage. An underlying sand bed and perforated drainage pipe system removes vertical seepage during the deposition phase, and the main embankment incorporates a pervious upstream zone to continuously decant precipitation and supernatant water. The seepage and supernatant water is pumped to lined water reservoirs at the mill site where the water is used as process water or treated for removal of radium, the only contaminant present.

4.0 NICKEL AND ARSENIC BALANCE

4.1 DETAILS

A nickel and arsenic metallurgical balance was derived for the Key Lake mill circuit to identify the dissolution of nickel and arsenic minerals in the Key Lake leaching circuit and to estimate the deportment of both elements in downstream uranium recovery and waste treatment circuits. The detailed balance is provided in Figure 4-1. The process flows shown in this flowchart represent the current Key Lake milling circuit as described in the previous section.

The main criteria used in calculating the metallurgical balance are listed in Table 4-1. The majority of the values given in this table are based on, or have been calculated from, plant values which can be considered typical of the Key Lake mill circuit.

The average ore grade of 1.9% Ni and 1.2% As is the average value of the Gaertner ore for the production period January 1985 to April 1986. A nominal ore throughput of 30 tonnes per hour has been used in the calculations but the actual tonnage of ore processed through the Key Lake circuit will vary depending on uranium ore feed grades to the mill. Tonnage throughput is varied to maintain the Key Lake annual production target of 5,443,200 kg U_3O_8 (12,000,000 lbs U_3O_8).

The average total nickel and arsenic dissolution in the Key Lake leaching circuit was taken as 55% and 60% respectively (Neven et al., 1985). These are average values and variations from these values can be expected depending on leaching conditions and the characteristics of the ore being processed.

The minewater analysis of 6 mg/L Ni and 3.5 mg/L As are typical values for minewater at Key Lake. The levels of nickel and arsenic in minewater can be expected to vary depending on the contact time of pitwater with ore and the nickel/arsenic content of the ore. The treated effluent analysis of 0.3 mg/L Ni and 0.05 mg/L As are levels that are regularly being achieved or exceeded in the Key Lake waste treatment circuit.

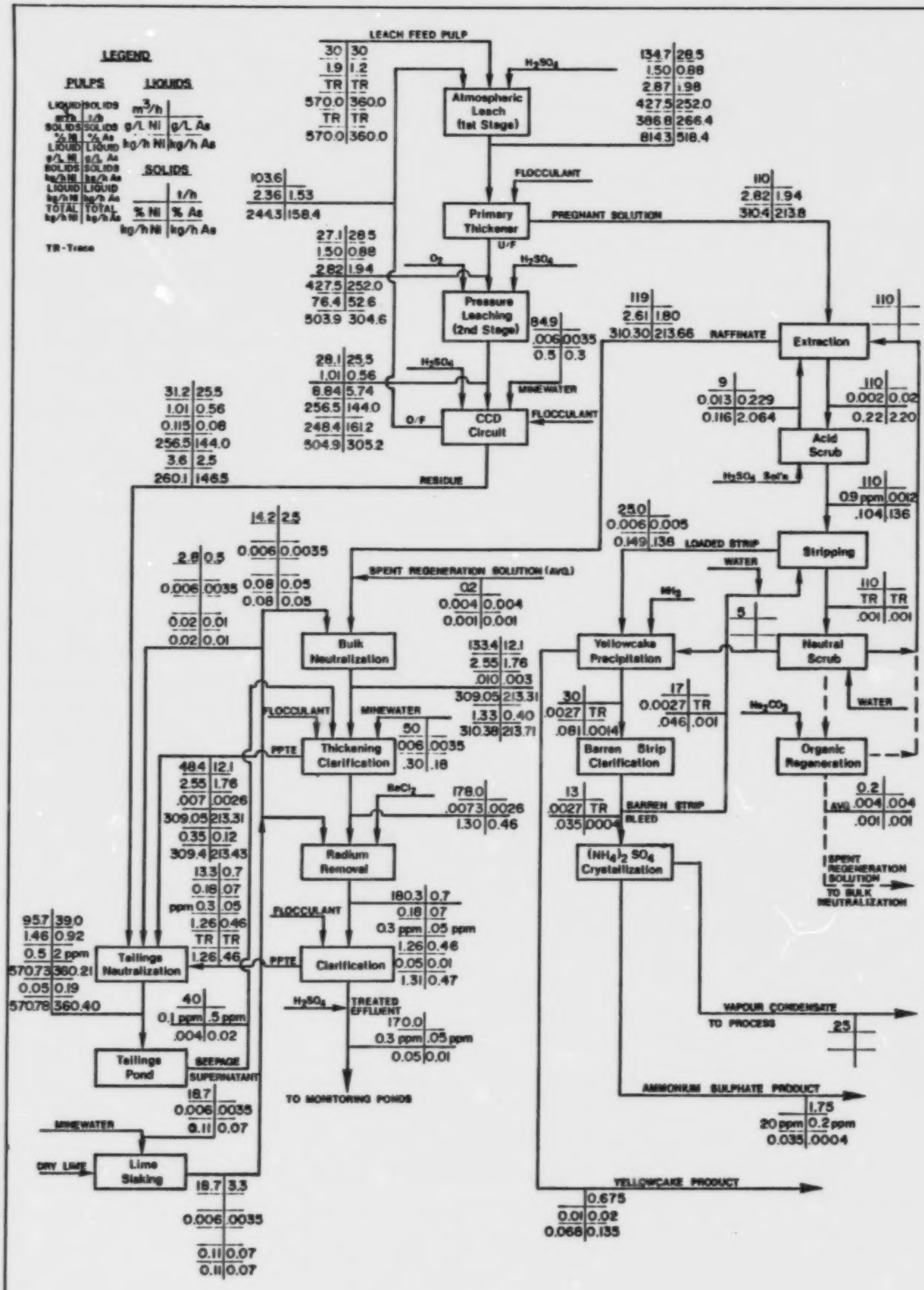

LEGEND
PULPS
LIQUIDS
SOLIDS
TR - Trace
LEACH FEED PULP
H_2SO_4
Atmospheric Leach (1st Stage)
FLOCCULANT
Primary Thickener
PREGNANT SOLUTION
U/F
O_2
Pressure Leaching (2nd Stage)
MINEWATER
CCD Circuit
O/F
RESIDUE
RAFFINATE
Extraction
Acid Scrub
H_2SO_4 Sol'n
Stripping
LOADED STRIP
WATER
NH_3
Yellowcake Precipitation
Neutral Scrub
Na_2CO_3
Organic Regeneration
SPENT REGENERATION SOLUTION TO BULK NEUTRALIZATION
SPENT REGENERATION SOLUTION (AVG.)
Bulk Neutralization
Thickening Clarification
PPTE
$BaCl_2$
Radium Removal
Clarification
TREATED EFFLUENT
TO MONITORING PONDS
Barren Strip Clarification
BARREN STRIP BLEED
$(NH_4)_2SO_4$ Crystallization
VAPOUR CONDENSATE TO PROCESS
AMMONIUM SULPHATE PRODUCT
YELLOWCAKE PRODUCT
Tailings Neutralization
Tailings Pond
SEEPAGE
SUPERNATANT
Lime Slaking
DRY LIME

FIGURE 4-1

NICKEL/ARSENIC METALLURGICAL BALANCE

KEY LAKE MILLING CIRCUIT

MELIS CONSULTING ENGINEERS LTD.

TABLE 4-1

BASIS OF NICKEL AND ARSENIC BALANCE

Ore leach feedrate (tonnes/hour)	- 30
Average oregrade - % Ni	- 1.9
- % As	- 1.2
Nickel dissolution (%) - total	- 55
- primary leach	- 25
- secondary leach	- 30
Arsenic dissolution (%) - total	- 60
- primary leach	- 30
- secondary leach	- 30
Weight loss in leach (%) - primary	- 5
- secondary	- 10
Primary and secondary leach feed density (% solids)	- 50
Pregnant solution/ore ratio (w/w)	- 3.85
Pregnant solution specific gravity	- 1.05
CCD wash efficiency (%)	- 99
CCD tails pulp density (% solids)	- 45
Organic flow (m^3/h)	-110
Loaded organic before acid scrub (g/L) - Ni	- 0.002
- As	- 0.020
Lime consumption (kg/t) - CCD tails	- 16
- bulk neutralization stage 1	- 84
- bulk neutralization stage 2	- 10
Minewater analysis (mg/L) - Ni	- 6
- As	- 3.5
Excess minewater to bulk neutralization (m^3/h)	- 50
Seepage and supernatant analysis (mg/L) - Ni	- 0.1
- As	- 0.5
Seepage and supernatant flow (m^3/h)	- 40
Neutralized tailings slurry liquid analysis (mg/L) - Ni	- 0.5
- As	- 2.0
Bulk neutralization stage 1 discharge analysis (mg/L) - Ni	- 10
- As	- 3

TABLE 4-1 continued

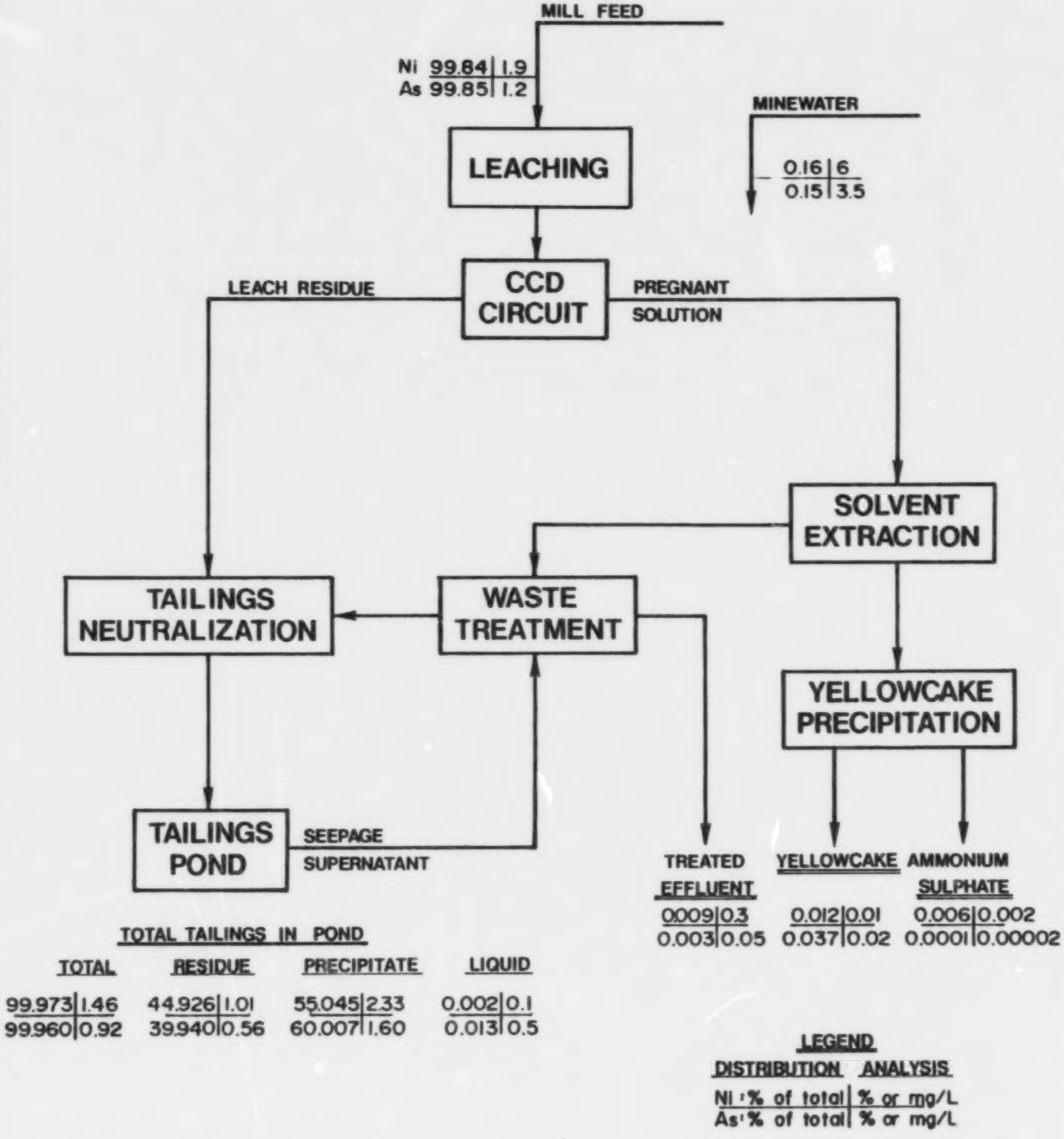
Treated effluent analysis (mg/L)	- Ni	- 0.3
	- As	- 0.05
Waste precipitate produced (t/h)	- CCD tails	- 0.7
	- bulk neutralization stage 1	- 12.1
	- bulk neutralization stage 2	- 0.7
Total tailings (tonnes/hour)		- 39.0
Yellowcake production (kg/h)		-675
Yellowcake analysis (%)	- Ni	- 0.01
	- As	- 0.02
	- U_3O_8	- 97
Ammonium sulphate production (kg/h)		- 1.75
Ammonium sulphate analysis (ppm)	- Ni	- 20
	- As	- 0.2

4.2 SUMMARY

A summary of the nickel/arsenic metallurgical balance calculated for the Key Lake circuit is presented in Figure 4-2. The distribution of nickel and arsenic in the main product and discharge streams are given as a percentage of the total nickel and arsenic fed to the circuit. The nickel and arsenic feed to the mill circuit is mainly the ore feed but there is also a minor contribution from minewater used as process water in the circuit or treated as excess water. Analysis of the main streams shown in this summary are given as percent or mg/L concentration.

The yellowcake product and ammonium sulphate by-product account for 0.018% of the total nickel and 0.037% of the total arsenic fed to the mill. The treated effluent, discharged at 0.3 mg/L Ni and 0.05 mg/L As, accounts for 0.009% of the total nickel and 0.003% of the total arsenic.

The combined neutralized tailings discharged to the tailings pond from the mill circuit, which include leach residue, waste precipitates and porewater, account for the remaining 99.973% of the nickel and 99.960% of the arsenic. Of this total reporting to the tailings pond 55.045% and 60.007% has been calculated as the amount of nickel and arsenic present in the tailings as chemical precipitates respectively. The nickel and arsenic present in the tailings as leach residue, which can be assumed to be undissolved nickel/arsenic minerals, is calculated at 44.926% and 39.940% respectively. The liquid contained in wet-settled tailings, which is assumed to be of the same analysis of seepage and supernatant water used in the metallurgical balance calculations, accounts for the remaining 0.002% of the nickel and 0.013% of the arsenic.


MILL FEED
Ni 99.84 | 1.9
As 99.85 | 1.2
MINEWATER
0.16 | 6
0.15 | 3.5
LEACHING
CCD CIRCUIT
LEACH RESIDUE
PREGNANT SOLUTION
SOLVENT EXTRACTION
TAILINGS NEUTRALIZATION
WASTE TREATMENT
YELLOWCAKE PRECIPITATION
TAILINGS POND
SEEPAGE
SUPERNATANT
TREATED EFFLUENT
0.009 | 0.3
0.003 | 0.05
YELLOWCAKE
0.012 | 0.01
0.037 | 0.02
AMMONIUM SULPHATE
0.006 | 0.002
0.0001 | 0.00002

TOTAL TAILINGS IN POND

TOTAL		RESIDUE		PRECIPITATE		LIQUID	
99.973	1.46	44.926	1.01	55.045	2.33	0.002	0.1
99.960	0.92	39.940	0.56	60.007	1.60	0.013	0.5

LEGEND

	DISTRIBUTION	ANALYSIS
Ni	% of total	% or mg/L
As	% of total	% or mg/L

FIGURE 4-2

NICKEL/ARSENIC BALANCE SUMMARY

5.0 LABORATORY TESTWORK

5.1 GENERAL

The laboratory testwork component of the study was carried out to establish the chemistry of the Key Lake waste treatment circuit in terms of nickel and arsenic precipitation. Precipitation of Key Lake raffinate at different pH values was accomplished to produce precipitates and associated filtrates which were submitted for chemical analysis. The precipitates were also examined mineralogically to attempt to determine the nature of the chemical precipitates produced. A separate test was also accomplished to simulate the Key Lake waste treatment circuit under treatment conditions used for the mill waste solutions at Key Lake. This afforded a precipitate produced under laboratory conditons with the same characteristics as the waste precipitates produced in The Key Lake circuit. An additional test was carried out on synthetic solutions to identify the relationships between arsenic and aluminum precipitation with solution concentrations typical of the Key Lake raffinate.

The experimental data generated was then interpreted and analysed in chemical modelling studies to predict the precipitation-dissolution mechanisms for nickel and arsenic in uranium mill tailings.

5.2 SAMPLE DESCRIPTION

The liquid samples required for test purposes were taken from the Key Lake mill circuit on the weekend of May 10, 1986 and were received at SRC in Saskatoon on May 23, 1986. The following solutions were received:

Solvent extraction raffinate	- 200 L
Minewater	- 20 L
Seepage and supernatant	- 20 L
Spent regeneration solution	- 10 L

Analyses of each liquid, filtered through a 3 micron millipore filter, are presented in Table 5-1. The raffinate solution was used in all precipitation tests. The other three liquids were only used in the test for simulating the Key Lake waste treatment circuit.

When reviewing these analyses it should be remembered that the solutions are grab samples and as such the analyses given cannot be considered as average values for the Key Lake circuit. This fact is exemplified by the nickel and arsenic assays of the raffinate, 3.3 g/L and 2.7 g/L respectively, which are greater than the nickel/arsenic assays calculated for raffinate in the mass balance detailed in Figure 4-1.

An arsenic speciation analysis performed by the Key Lake analytical laboratory gave an As(III)/As(V) ratio of 7 to 1 for the raffinate. This value is substantially greater than a previously reported ratio of 1 to 1 (Neven et al., 1985). Discussions with Key Lake metallurgical staff confirmed that arsenite/arsenate ratios will vary depending on circuit conditions and that a ratio of 7/1, although surprising, is not unexpected.

TABLE 5-1
KEY LAKE SOLUTION ANALYSES (mg/L)

Element	Raffinate	Minewater	Seepage and Supernatant	Spent Regeneration Solution
Ni	3,300	12	0.094	0.94
As	2,700	0.07	0.55	5.7
Ca	950	51	360	9.0
Mg	840	13	9.3	3.8
Fe	2,100	0.21	0.035	2.0
Al	1,000	0.73	0.27	0.62
Cu	46	0.044	<0.005	0.11
Pb	0.16	-	-	-
Zn	110	0.47	0.012	0.012
SiO_2	680	13.5	8.1	5.6
SO_4	33,200	200	905	9,060
PO_4	810	-	-	-
As(III)	2,360*	-	-	-
As(V)	340*	-	-	-

* based on an arsenic speciation analysis giving an As(III)/As(V) ratio of 7 to 1

5.3 TEST METHODOLOGY AND RESULTS

5.3.1 General

The main purpose of the laboratory testwork component of the study was to produce chemical precipitates to assess the precipitation mechanisms of nickel and arsenic during neutralization of raffinate. These tests also afforded information on solution chemistry which would identify the deportment of nickel and arsenic in conjunction with other major ions in solution.

A total of twelve precipitation tests were accomplished on raffinate solution. Seven precipitates were produced at increasing pH values, one precipitate was produced in the pH range 5 to 7, and four precipitates were produced at pH 9 under different reaction times.

A single neutralization test was completed to simulate the Key Lake waste treatment circuit. In this test two precipitates were produced, one at pH 7 and one at pH 11.

Precipitation of synthetic solutions were also accomplished to produce precipitate reference standards for mineralogy examination and to assess the co-precipitation of arsenic and aluminum.

In each test the solution was mechanically agitated with a laboratory stirrer during the lime neutralization stage. Flocculant was added to coagulate the precipitate prior to filtration. All filtrate samples were filtered through a 3 micron millipore filter prior to analysis. The precipitates produced were dried overnight in an air-circulating oven at a temperature of 50-70°C.

5.3.2 Raffinate Precipitation

Pre-Neutralization

Previous work (Knight and Piesold et al., 1985) had shown that the presence of large amounts of gypsum relative to other forms of precipitates made it extremely difficult, if not impossible, to determine the composition of the different complexes formed in neutralization. To partially overcome this masking problem by calcium sulphate a large batch of raffinate (40 L) was first neutralized to pH 2 with hydrated lime slurry to precipitate a portion of the gypsum from the raffinate.

Neutralization of the raffinate was carried out at room temperature in a 20 L plastic container by the addition of a hydrated lime slurry to a mechanically agitated raffinate solution. After neutralization a 4 ppm dosage of anionic polyacrylamide flocculant (Percol E-24) was added as a 1 g/L solution and the precipitate slurry allowed to settle overnight prior to filtering the gypsum precipitate from the solution. The precipitation conditions used in pre-neutralization of the raffinate are summarized in Table 5-2. Solution and precipitate analyses for this preneutralization step are given in Table 5-3.

The lime consumed in adjusting the pH of the raffinate from 1.0 to 1.95 was 11.5 g $Ca(OH)_2$ (100%)/L of raffinate feed. This resulted in a total of 31.4 g of gypsum precipitate being produced per litre of raffinate. Solution analyses indicated that approximately 20% of the arsenic was co-precipitated with the gypsum leaving a raffinate solution containing 2.1 g/L As. Although product analyses indicate that about 4% of the nickel was co-precipitated with the gypsum comparison of the filtrate analysis (3.4 g/L Ni) to the original raffinate analysis (3.3 g/L Ni) shows that nickel co-precipitation was negligible during gypsum removal.

The sulphate and calcium assays indicated that a substantial amount of gypsum remained dissolved or as colloidal particles after neutralizing the raffinate to pH 2. Subsequent mineralogical work revealed that large quantities of gypsum were in fact present in the precipitates produced under increasing pH conditions.

Precipitation at Different pH Values

To examine the effect of pH on the quantity and composition of precipitates formed, a series of precipitates were produced at different pH values. The pH 2 raffinate solution generated in the pre-neutralization step above was neutralized with lime at room temperature to pH values increasing from 5 to 11. A 2 L volume of raffinate was used in each test with sufficient lime slurry being added to attain the required pH. The precipitated slurry was

TABLE 5-2
GYPSUM PRECIPITATION CONDITIONS

Total raffinate volume (L)		-	40
Initial pH		-	1.0
Precipitation pH		-	1.95
Lime (100% $Ca(OH)_2$) added	- g		459
	- g/L		11.5
Temperature (°C)		-	25
Reaction time (hours)		-	4
Flocculant - type		-	Percol E-24
- dosage (mg/L)		-	4
Gypsum precipitate produced	- g	-	1256.1
	- g/L	-	31.4

TABLE 5-3
GYPSUM PRECIPITATION ANALYSES

	Raffinate Feed (mg/L)	Filtrate (mg/L)	Precipitate (%)
pH	1.0	1.95	-
Ni	3,300	3,400	0.5
As	2,700	2,100	1.70
Ca	950	690	19.3
Mg	840	890	0.14
Fe	2,100	1,900	1.10
Al	1,000	1,100	0.25
Cu	46	47	0.014
Pb	0.16	0.03	-
Zn	110	110	-
SiO_2	680	810	0.25
SO_4	33,200	20,800	42.4
PO_4	810	640	-

allowed to mix for 1 hour after which 5 ppm of Percol E-24 flocculant was added. The settled precipitate was then filtered, dried and submitted for analysis along with the filtrate solution. Lime additions and the weight of precipitates produced from each test are given in Table 5-4. Test results are summarized in Tables 5-5, 5-6, 5-7 and 5-8.

The amount of precipitate produced in the neutralization of raffinate increases from 31.4 g/L at pH 2 to 89.8 g/L at pH 11. This trend is depicted in Figure 5-1.

Material balances have been calculated from the test results of each test to arrive at cumulative removal efficiencies of major elements. These removal efficiencies, given in Table 5-8, are depicted in Figures 5-2 and 5-3 and 5-4.

An assessment of the results from the pH variation tests has provided trends of chemical behaviour for consideration in the geochemical modelling component of the study. The behaviour of nickel indicates that a minor amount is precipitated at pH 2 with virtually all the nickel present precipitated from solution at pH 9. On the other hand approximately 20% of the arsenic was removed with the gypsum in the pH 2 pre-neutralization step and by pH 5 arsenic precipitation was essentially complete. Nickel seems to be removed from solution independently of any other elements. The majority of the nickel (85%) is precipitated between pH 5 and pH 7.

Magnesium precipitation increases gradually from pH 2 to pH 11. The largest amount of magnesium is precipitated between pH 7 and pH 11 which exemplifies the importance of magnesium precipitation in the Key Lake waste treatment circuit as a co-precipitator for trace levels of arsenic and heavy metals.

Iron and zinc precipitation was found to be complete at pH 7 whereas aluminum precipitation was virtually complete at pH 5.

TABLE 5-4
RAFFINATE PRECIPITATION CONDITIONS*
pH VARIATION

pH	Reaction Time (h)	$Ca(OH)_2$ (100%) Added (g/L)	Precipitate Produced (g/L)
2 to 5	1	7.3	25.0
2 to 6	1	11.3	37.15
2 to 7	1	15.1	47.35
2 to 8	1	19.8	53.5
2 to 9	1	16.3	54.8
2 to 11	1	19.5	58.35

* feed for each test was pre-neutralized raffinate at pH 2, all tests were done at room temperature.

TABLE 5-5
RAFFINATE PRECIPITATION RESULTS
pH VARIATION
FILTRATE ANALYSES (mg/L)

Element	pH 1*	pH 2	pH 5	pH 6	pH 7	pH 8	pH 9	pH 11
Ni	3,300	3,400	3,000	1,600	13	2.6	0.61	0.54
As	2,700	2,100	3.3	3.2	4.5	5.8	3.9	3.1
Ca	950	690	560	540	570	610	700	740
Mg	840	890	840	820	580	480	40	1.5
Fe	2,100	1,900	910	0.96	0.07	0.09	0.23	0.12
Al	1,000	1,100	7.7	<0.02	0.08	0.03	0.83	13
Cu	46	47	3.8	<0.005	<0.005	<0.005	0.007	<0.005
Pb	0.16	0.03	0.28	<0.02	<0.02	<0.02	<0.02	<0.02
Zn	110	110	5.3	0.65	0.01	<0.005	<0.005	<0.005
SiO_2	680	810	110	21	8.6	1.9	0.9	1.1
SO_4	33,200	20,800	10,600	6,980	4,130	3,330	1,900	1,630
PO_4	810	640	2.0	1	0.93	0.55	0.78	0.64

* raffinate as received

TABLE 5-6
RAFFINATE PRECIPITATION RESULTS
pH VARIATION
PRECIPITATE ANALYSES (%)

	pH							
Element	1 to 2	2 to 5	2 to 6	2 to 7	2 to 8	2 to 9	2 to 11	5 to 7
Ni	0.50	1.48	3.92	5.64	5.05	5.40	4.73	13.7
As	1.70	7.55	5.80	4.15	3.80	4.00	3.65	0.01
Ca	19.3	13.5	14.7	16.7	18.4	16.8	17.5	12.0
Mg	0.14	0.20	0.28	0.52	0.75	1.49	1.39	0.38
Fe	1.10	3.86	4.68	3.54	3.24	3.48	3.12	6.06
Al	0.25	3.50	2.60	2.20	1.90	2.10	1.70	-
SiO_2	0.25	2.64	2.26	1.85	1.74	1.61	1.61	1.21
SO_4	42.4	34.1	35.7	32.7	30.8	33.0	31.5	33.2

TABLE 5-7
RAFFINATE PRECIPITATION RESULTS(1)
pH VARIATION
Ni/As DISTRIBUTIONS (%)(2)

	Ni		As	
pH	Filtrate	Precipitate	Filtrate	Precipitate
2 to 5	89.0	11.0	0.2	99.8
2 to 6	52.4	47.6	0.15	99.85
2 to 7	0.5	99.5	0.2	99.8
2 to 8	0.1	99.9	0.3	99.7
2 to 9	0.02	99.98	0.2	99.8
2 to 11	0.02	99.98	0.15	99.85

(1) feed was pre-neutralized raffinate at pH 2
(2) distributions based on product analyses

TABLE 5-8
RAFFINATE PRECIPITATION RESULTS
pH VARIATION
CUMULATIVE REMOVAL EFFICIENCIES OF MAJOR ELEMENTS*

Element	pH 2	pH 5	pH 6	pH 7	pH 8	pH 9	pH 11
Ni	4.4	14.9	49.9	99.5	99.9	99.98	99.98
As	20.3	99.8	99.88	99.84	99.76	99.84	99.88
Mg	4.7	10.0	15.5	33.1	48.2	95.5	99.8
Fe	15.4	59.0	99.96	99.99	99.99	99.99	99.99
Al	6.7	99.2	>99.99	99.99	>99.99	99.93	98.8
Zn	0	95.2	99.4	99.99	>99.99	>99.99	>99.99
SiO_2	10.0	88.6	98.0	99.3	99.8	99.9	99.9
SO_4	39.0	66.2	68.7	87.1	89.8	94.2	95.1
PO_4	21.0	99.8	99.9	99.9	99.9	99.9	99.9
Precipitate g/L	31.4	56.4	68.6	78.8	84.9	86.2	89.8

* calculations for Ni, As, Mg, Fe, Al, SiO_2, SO_4 are based on product analyses and calculations for Zn and PO_4 are based on raffinate feed and filtrate analyses.

FIGURE 5-1
pH VARIATION TESTS
PRECIPITATE PRODUCED VS pH

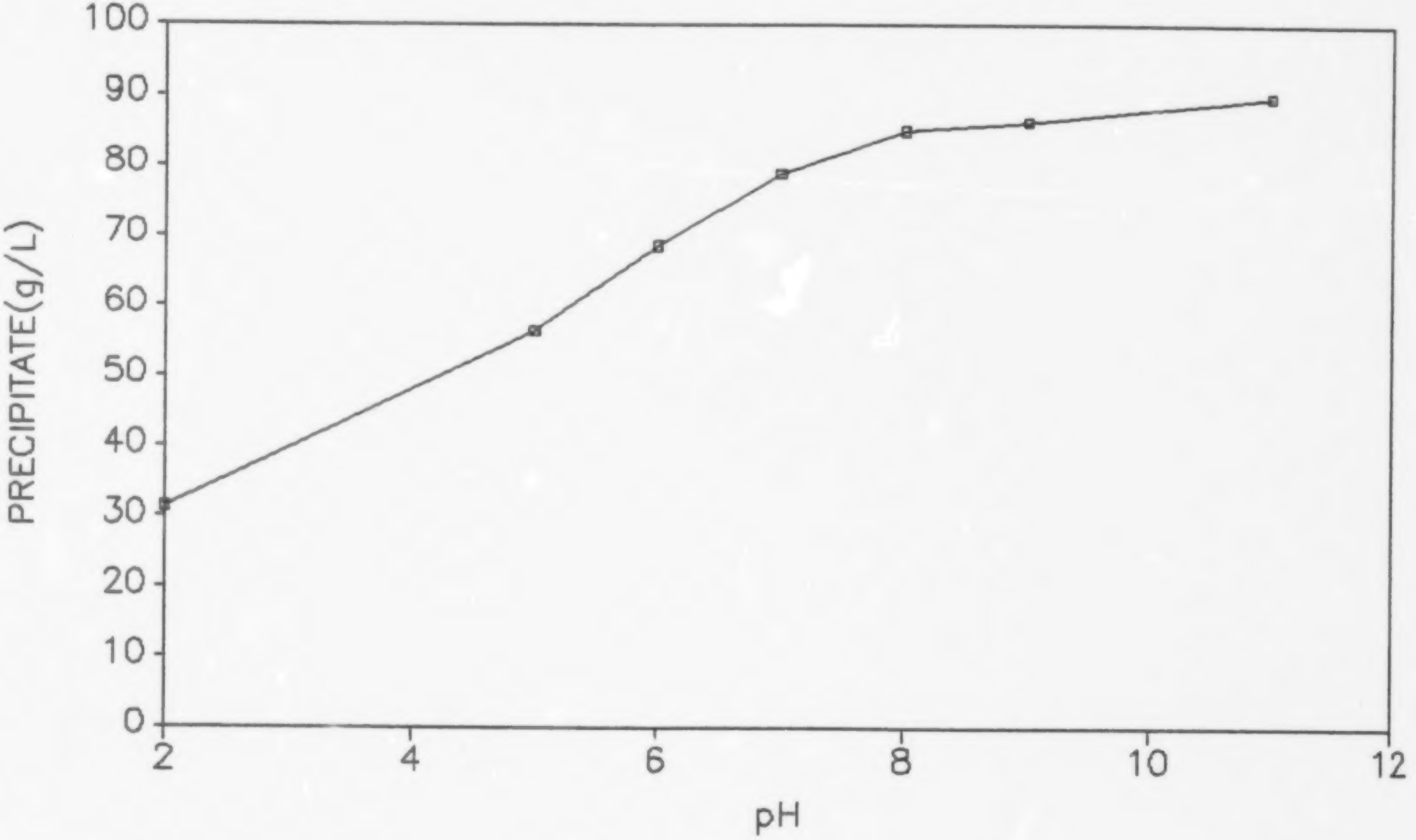


FIGURE 5–2
pH VARIATION TESTS
As,Al,PO4 REMOVAL EFFICIENCIES

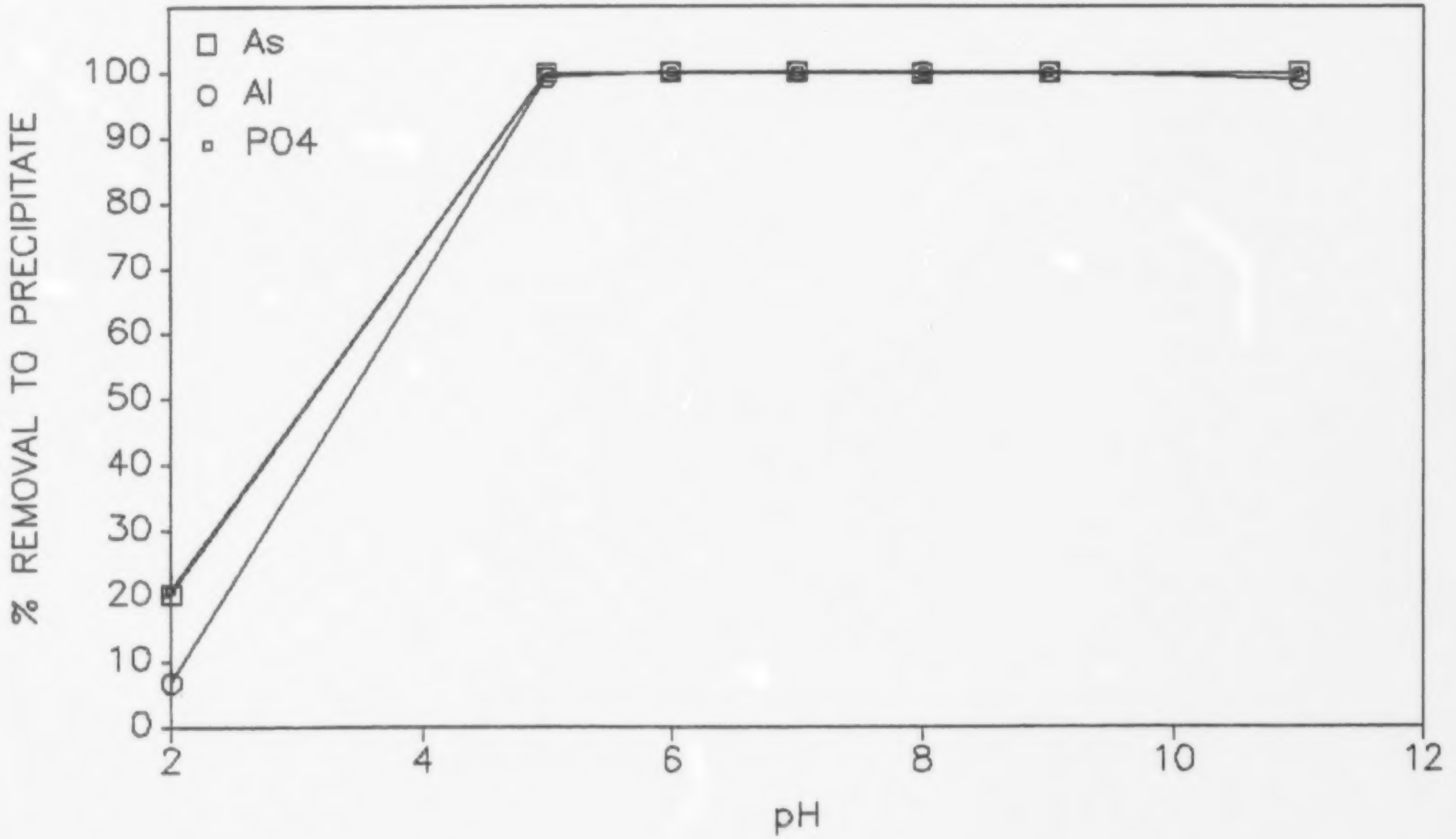


FIGURE 5–3
pH VARIATION TESTS
Ni,Mg,Fe REMOVAL EFFICIENCIES

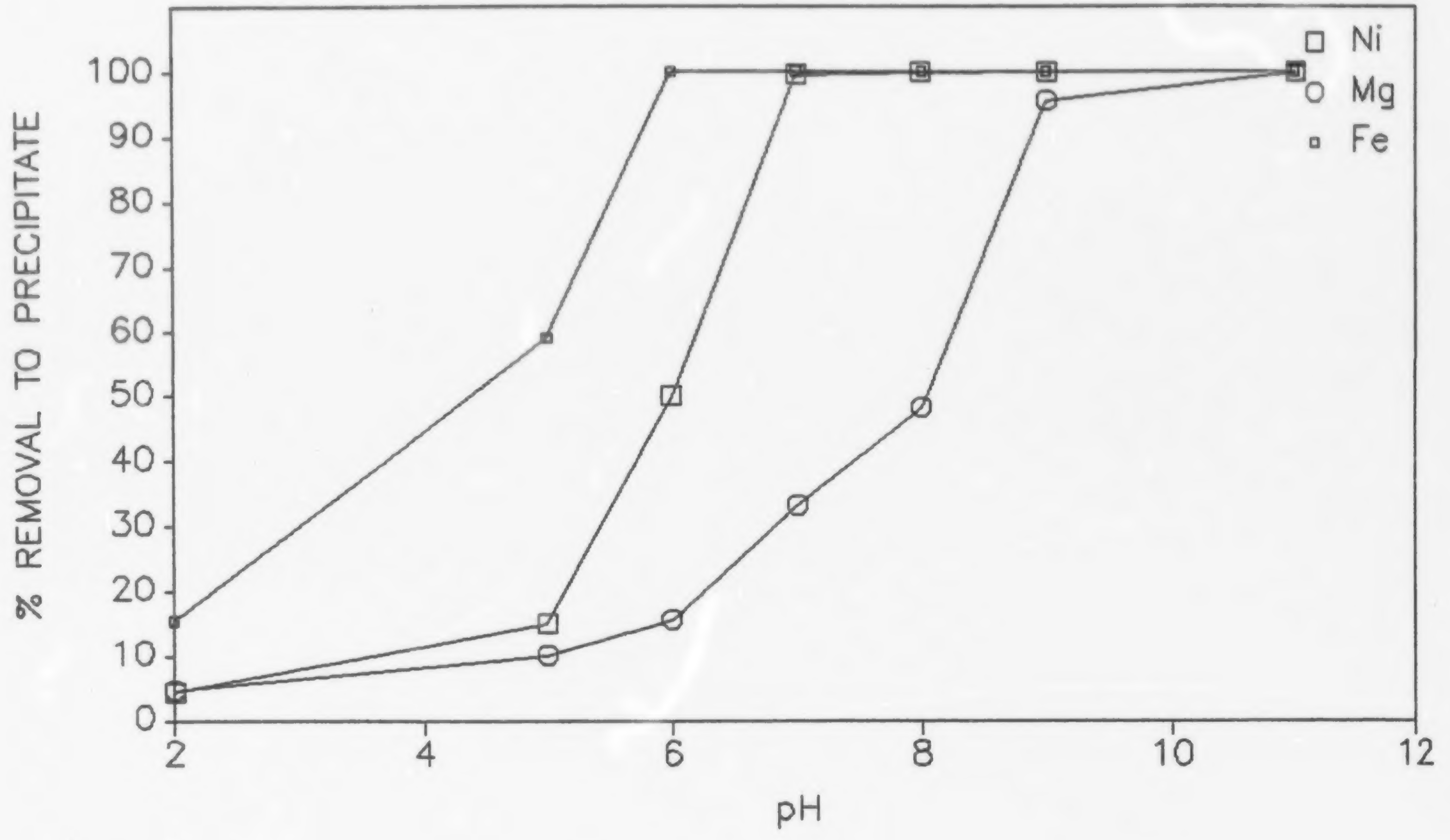
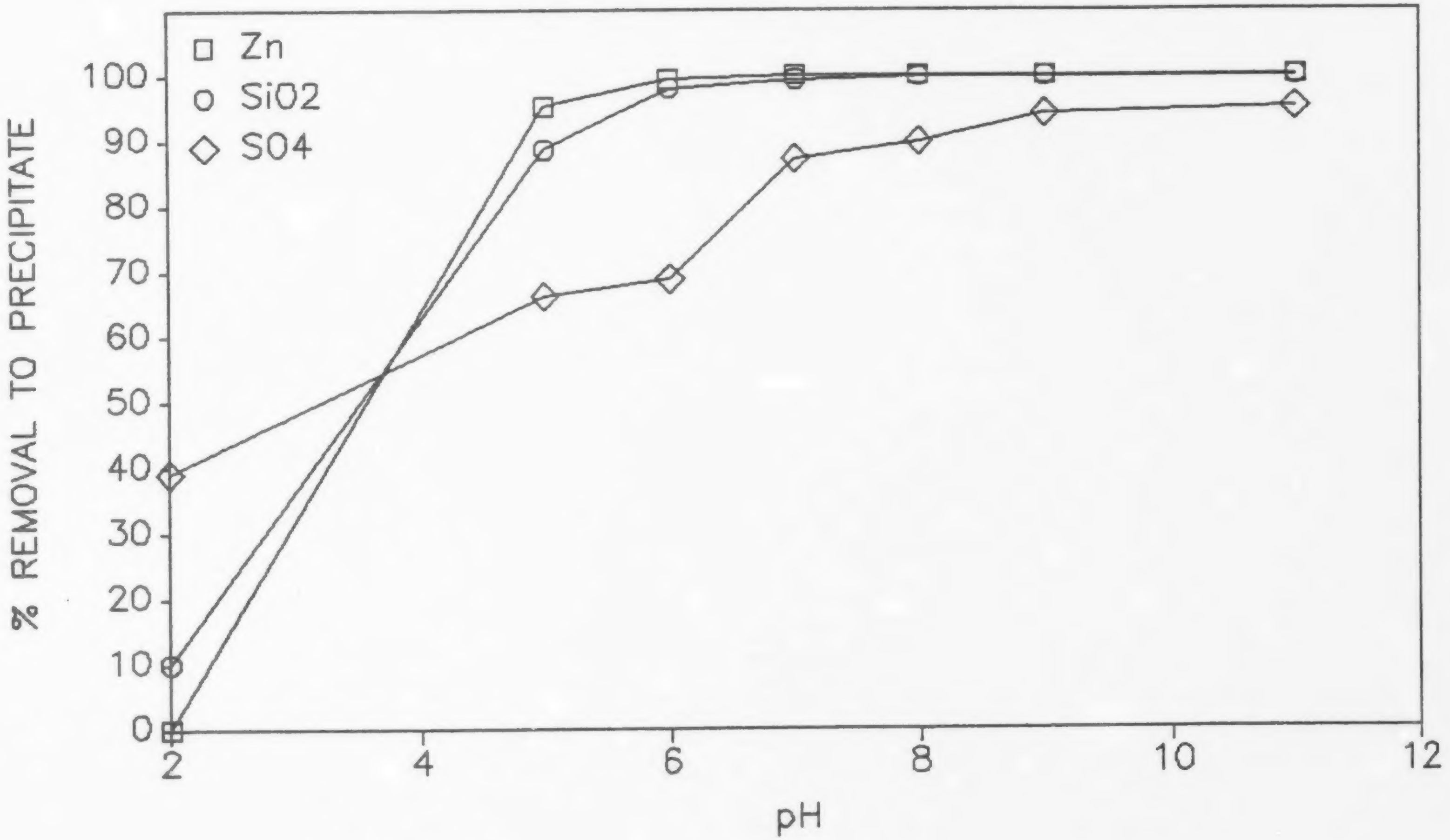


FIGURE 5–4
pH VARIATION TESTS
Zn,SiO2,SO4 REMOVAL EFFICIENCIES



Silica continues to precipitate up to pH 9 while sulphate precipitation, which is controlled by the solubility of gypsum in solution, is evident up to pH 11. Phosphate removal also increases gradually to pH 11.

Arsenic, aluminum and phosphate precipitation occurs at the same pH values with all three precipitated from solution at pH 5. The concurrent precipitation of these three elements is evident from the graph drawn in Figure 5-2.

In general the cations are precipitating at pH values typical for their pure hydroxide forms with the exception of iron and aluminum. Aluminum seems to be precipitating before iron whereas the precipitation pH for iron and aluminum trivalent hydroxides in pure solutions are 2.8 to 3 and 3.5 to 4 respectively.

As observed the majority of the nickel is removed from the raffinate between pH 5 and pH 7 and an insignificant amount of arsenic remains in this pH range. A separate precipitate was therefore produced in this pH range by neutralizing pH 5 filtrate to pH 7 with lime. This afforded a high nickel-low arsenic precipitate for chemical analyses and mineralogical examination. The chemical analysis of this precipitate is given in Table 5-6. The high nickel content in the precipitate is evident from the analysis.

Precipitation for Varying Times

Since reaction time, or contact time with mother liquor, is considered an important variable in the formation of chemical precipitates during neutralization, a series of neutralization tests were completed at four different reaction times.

A portion of the raffinate "as-received" was neutralized to pH 2 as described above to produce a second batch of pre-neutralized raffinate. This raffinate filtrate was subsequently neutralized to pH 9 in four separate tests and the pH-adjusted slurry allowed to react for 0.5, 2, 6 and 24 hours. At the end of the reaction time the precipitate and filtrate from each test was collected and submitted for analysis.

Lime addition along with the weight of precipitate produced for each test are summarized in Table 5-9. Analysis of the pre-neutralized raffinate feed, filtrates and precipitates for each test are given in Table 5-10. Nickel and arsenic distributions calculated from these results are listed in Table 5-11.

The amount of precipitate produced for the 0.5-hour retention time was slightly less that the three longer reaction times of 2, 6 and 24 hours. This lower amount of precipitate is reflected in the filtrate assays for Mg and SO_4 which showed a lower removal of these two species from solution for the 0.5-hour test.

Nickel and arsenic distributions to the precipitate are depicted graphically in Figure 5-5. The nickel removed to the precipitate was consistent for all four reaction times with greater than 99.9% being removed in each test. Arsenic on the other hand showed a definite trend of re-solubilization with increasing reaction time. The filtrate assay increased from 0.3 mg/L As for the 0.5-hour test to 0.8 mg/L As for the 24-hour test. This would indicate that the precipitated arsenic tends to go back into solution with extended reaction time although additional work would be required to confirm this observation.

Key Lake Waste Treatment Circuit Simulation Test

A simulation of the Key Lake waste treatment circuit was completed in one test under the general treatment conditions depicted in Figure 5-6. The treatment conditions used are generally based on the waste treatment process currently being operated at Key Lake. The volumes of liquid waste solutions added were based on the flowrates given in the nickel and arsenic balance detailed in Figure 4-1.

Analysis of the raffinate, spent regeneration solution, seepage and supernatant and minewater feed solutions have been previously given in Table 5-1. Analyses of the pH 7 and pH 11 filter cake as well as the final treated filtrate are given in Table 5-12.

TABLE 5-9
RAFFINATE PRECIPITATION CONDITIONS*
REACTION TIME VARIATION

Reaction Time (h)	pH	$Ca(OH)_2$ (100%) Added (g/L)	Precipitate Produced (g/L)
0.5	2 to 9	15.5	52.15
2	2 to 9	15.7	53.55
6	2 to 9	15.4	53.25
24	2 to 9	16.4	53.40

* feed was pre-neutralized raffinate at pH 2

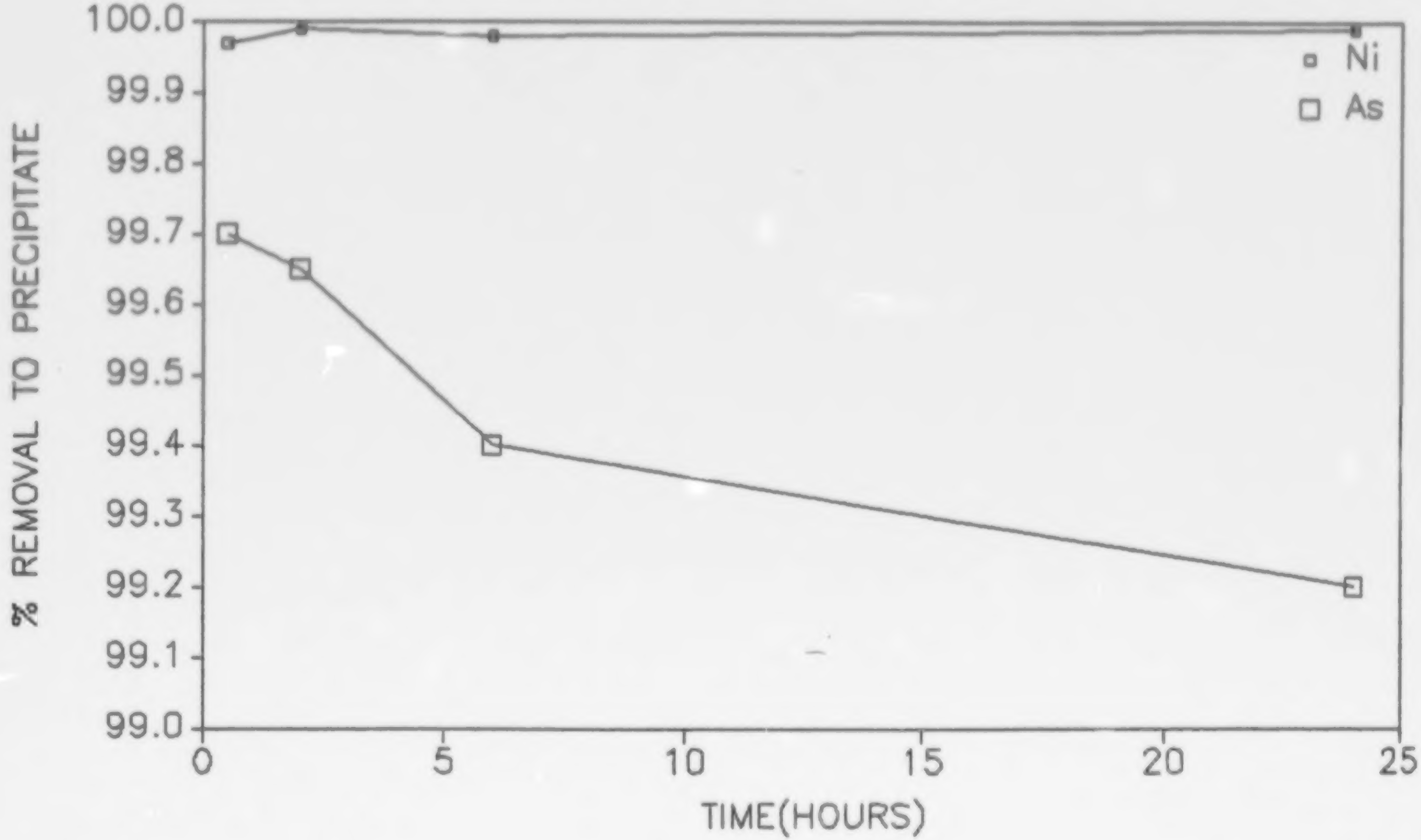
TABLE 5-10
RAFFINATE PRECIPITATION RESULTS
REACTION TIME VARIATION
FILTRATE AND PRECIPITATION ANALYSES

		Filtrate (mg/L)				Precipitate (%)			
Element	Feed	0.5 h	2 h	6 h	24 h	0.5 h	2 h	6 h	24 h
Ni	3,100	0.75	0.23	0.50	0.15	5.05	4.93	4.72	4.83
As	2,200	5.6	7.7	12	18	4.0	4.10	3.80	4.10
Ca	670	690	660	610	650	15.6	15.2	15.4	15.7
Mg	820	300	130	200	140	0.93	1.23	1.24	1.30
Fe	1,900	0.08	0.11	0.14	0.15	3.21	3.23	3.27	3.11
Al	1,000	0.92	1.8	1.6	1.1	1.34	0.66	1.07	1.34
Cu	46	0.015	0.024	0.013	0.024	-	-	-	-
Zn	93	<0.005	<0.005	<0.005	<0.005	-	-	-	-
SiO_2	680	1.5	1.3	1.5	3.0	1.66	1.70	1.98	1.82
SO_4	20,500	2,850	2,000	2,050	1,870	34.6	36.0	35.2	34.5
Ppte g/L	-	-	-	-	-	52.15	53.55	53.25	53.40

TABLE 5-11
RAFFINATE PRECIPITATION RESULTS
REACTION TIME VARIATION
Ni/As DISTRIBUTIONS (%)

	Ni		As	
Time (h)	Filtrate	Precipitate	Filtrate	Precipitate
0.5	0.03	99.97	0.30	99.70
2	0.01	99.99	0.35	99.65
6	0.02	99.98	0.60	99.40
24	0.01	99.99	0.80	99.20

FIGURE 5–5
REACTION TIME VARIATION
NICKEL–ARSENIC REMOVAL



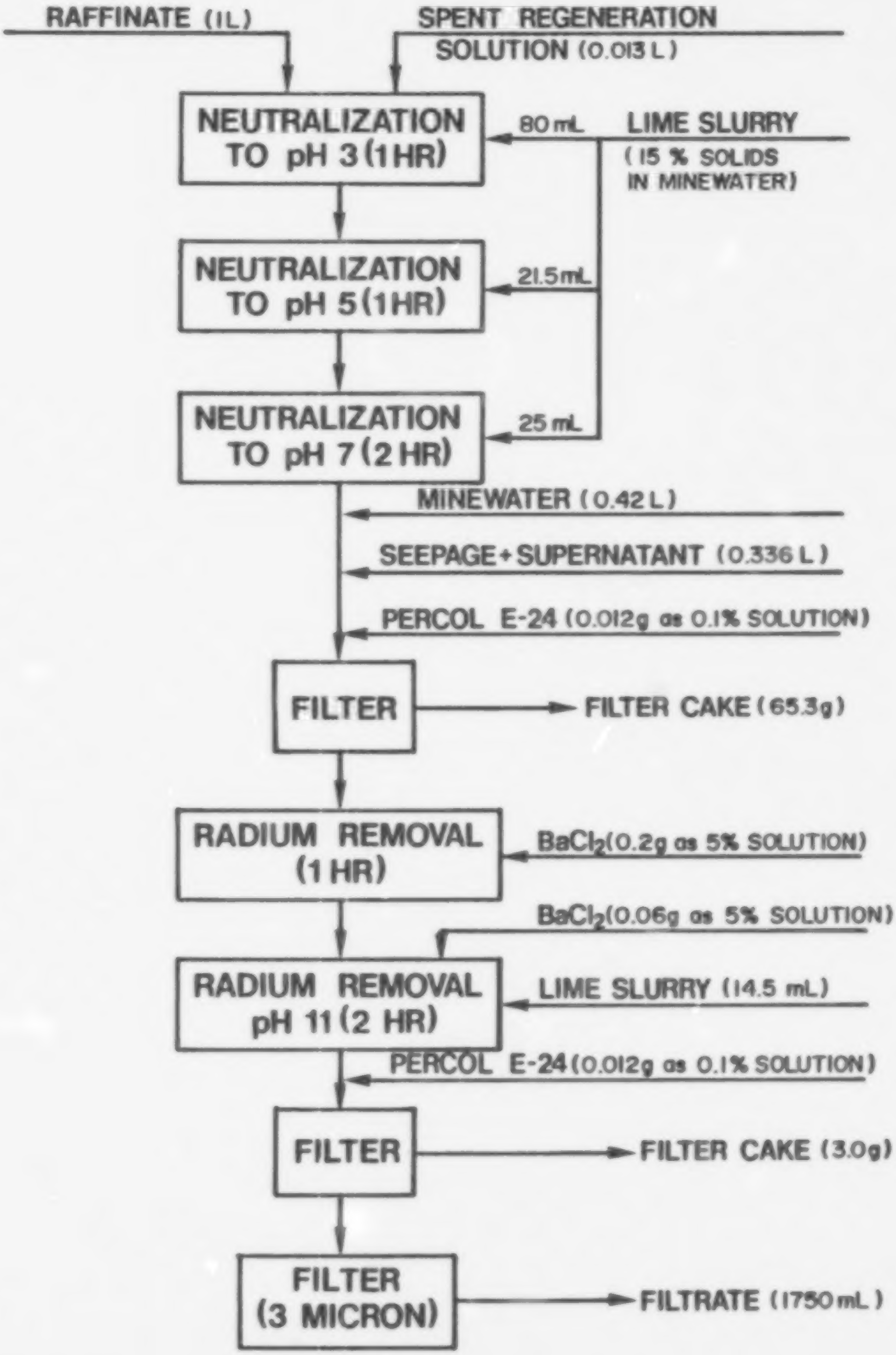

RAFFINATE (1L)
SPENT REGENERATION SOLUTION (0.013 L)
NEUTRALIZATION TO pH 3 (1 HR)
80 mL
LIME SLURRY (15 % SOLIDS IN MINEWATER)
NEUTRALIZATION TO pH 5 (1 HR)
21.5 mL
NEUTRALIZATION TO pH 7 (2 HR)
25 mL
MINEWATER (0.42 L)
SEEPAGE + SUPERNATANT (0.336 L)
PERCOL E-24 (0.012g as 0.1% SOLUTION)
FILTER
FILTER CAKE (65.3g)
RADIUM REMOVAL (1 HR)
BaCl2 (0.2g as 5% SOLUTION)
BaCl2 (0.06g as 5% SOLUTION)
RADIUM REMOVAL pH 11 (2 HR)
LIME SLURRY (14.5 mL)
PERCOL E-24 (0.012g as 0.1% SOLUTION)
FILTER
FILTER CAKE (3.0g)
FILTER (3 MICRON)
FILTRATE (1750 mL)

FIGURE 5-6

KEY LAKE WASTE TREATMENT SIMULATION TEST

TABLE 5-12
KEY LAKE SIMULATION TEST RESULTS

Element	Filter Cake (%) pH 7	pH 11	Final Filtrate (mg/L)
Ni	3.64	2.81	0.017
As	3.90	0.146	0.009
Ca	15.9	8.2	1,000
Mg	0.20	16.8	6.2
Fe	2.66	0.07	0.45
Al	1.12	0.09	0.07
Cu	-	-	<0.005
Zn	-	-	0.01
SiO_2	1.42	11.8	1.9
SO_4	42.3	10.4	2,340

The efficiency of the Key Lake waste treatment circuit in removing heavy metals and arsenic to exceptionally low levels is exemplified by the final filtrate analysis. Nickel and arsenic are reduced from g/L levels to 0.017 and 0.009 mg/L respectively. The almost complete removal of arsenic, aluminum and iron in the first stage bulk neutralization step is confirmed by the high filter cake assays at pH 7 and the low assay of the filter cake at pH 11. The importance of magnesium in the precipitation reaction above pH 7 is indicated by the high magnesium content of the pH 11 filter cake.

Material balances based on product analyses for nickel and arsenic show that 96.59% of the nickel and 99.84% of the arsenic are removed in the bulk neutralization step to pH 7. The remaining 3.41% and 0.16%, for nickel and arsenic respectively, are removed in the second stage treatment for radium removal.

Synthetic Solution Test

The similarity of arsenic and aluminum precipitation observed in the neutralization tests (see Figure 5-2) was investigated by completing arsenic and aluminum precipitation tests on synthetic solutions.

In the first test a 1 L synthetic arsenic solution assaying 2.1 g/L As was made up using $Na_2HAsO_4.7H_2O$ in deionized water. The pH was first adjusted to 1.9 with 50 g/L H_2SO_4. A total of 2.5 g of $CaSO_4.1/2H_2O$ was then added to saturate the solution with gypsum. The solution was stirred overnight and then filtered to remove any excess gypsum. The saturated gypsum filtrate was neutralized to pH 5 with lime slurry for 1 hour and the resulting precipitate removed by filtration. The clear filtrate was then submitted for arsenic analysis.

A second test was accomplished as above using a 2.1 g/L As synthetic solution but with 1.1 g/L Al also present in solution made up by the addition of $KAl(SO_4)_2.12H_2O$. The test procedure was the same as described above with the final filtrate being analysed for both arsenic and aluminum.

The weight of precipitate from the first test was only 0.3 g while the arsenic/aluminum test precipitate weighed 19.0 g. The filtrate from the first test analysed 2.2 g/L As which indicated virtually no removal of arsenic from solution. The filtrate from the second test assayed 49 mg/L As and 0.31 mg/L Al.

This synthetic solution test therefore strongly suggests that arsenate requires the presence of aluminum, or other suitable cations, in order to be precipitated from solution by the addition of lime. The observed trend of arsenic and aluminum precipitation occurring simultaneously in the neutralization of raffinate was confirmed by this synthetic solution test.

5.4 QUALITY ASSURANCE

The quality assurance program for the analytical component of the study consisted of several methods used routinely by SRC's analytical department. The following checks were done during analysis of the products generated in this study:

Blanks

Reagent and/or digestion blanks were carried through with each batch of samples submitted for analysis.

Standards

Standards were run at the beginning and end and between every tenth sample during a group of measurements. When a distillation or separation step is involved standards are carried through the entire procedure.

Controls

Internal Controls are prepared for water samples by spiking a water sample with the parameters being analysed. External controls available from the U.S. EPA, which cover a wide range of analytes, are run at random. For solid matrices certified reference materials are chosen to be as similar as possible to the samples submitted for analysis.

Duplicates

Every tenth sample in a batch or group of measurements is split and treated as two separate samples. If there are less than ten samples from one client, it may be another client's sample in the same batch of measurements that is split.

Interlaboratory Programs

SRC's analytical laboratory participates in several interlaboratory programs. These include analysis of major ions in water, metals in water, mercury in fish, PCB in sediment and radionuclides in water and ores.

Checking of Results

If a sample is from a group of samples that is routinely analyzed, results are compared to previous assays. Any results that are unusually high or low are rechecked. When all major ions are requested for analysis, an ion balance is calculated as another check.

6.0 MINERALOGICAL EXAMINATION OF PRECIPITATES

6.1 GENERAL

The thirteen precipitates prepared in the neutralization tests described above were examined mineralogically to attempt to identify the solid components formed. The mineralogical examination techniques employed included:

- optical microscope
- transmission electron microscope
- scanning electron microscope
- x-ray diffraction
- Raman microprobe.

The complete mineralogical report is detailed in Appendix B. For ease of reference the thirteen precipitates submitted for mineralogical examination were labelled as Precipitates No. 1 to No. 13 as listed in Table 6-1.

TABLE 6-1
LIST OF PRECIPITATES FOR MINERALOGICAL EXAMINATION

Precipitate No.	Precipitate Description
1	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 5 for 1 hour.
2	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 6 for 1 hour.
3	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 7 for 1 hour.
4	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 8 for 1 hour.
5	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9 for 1 hour.
6	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 11 for 1 hour.
7	Filter cake from filtrate obtained from treatment of No. 1 above taken to pH 7.
8	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9; with a 2-hour retention time.
9	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9; with a 6-hour retention time.
10	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9; with a 0.5-hour retention time.
11	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9; with a 24-hour retention time.
12	Stage 1 (pH 7) filter cake from the Key Lake waste treatment circuit simulation test.
13	Stage 2 (pH 11) filter cake from the Key Lake waste treatment circuit simulation test.

6.2 PHYSICAL CHARACTERIZATION

The thirteen precipitates were first examined with the optical microscope and by the scanning electron microscope (SEM).

A series of SEM photomicrographs were obtained for all thirteen precipitates and these are presented in Figures 1, 2 and 3 of Appendix B along with appropriate descriptions of each photomicrograph.

The SEM examination and visual observation with the optical microscope showed that Precipitates No. 1 to No. 12 consisted of the following constituents:

- abundant white needles, laths and plates of gypsum
- yellow-brown aggregates of sub-micron size tabular crystals adhering to or interstitial to gypsum crystals
- round nodules (pisoliths) up to 0.1 mm in diameter composed of a core of crystalline gypsum covered by a thin shell of yellow, brown or black sub micron size tabular crystals (in particular see Figure 3-C in Appendix B).

Based on the similarity of morphology and grain size the tabular crystals making up the yellow-brown aggregates, and the shells of pisoliths, are believed to be the same substance (see Figure 1-E in Appendix B).

Precipitate No. 13, the second-stage precipitate from the Key Lake waste treatment circuit simulation test, was entirely different to the other twelve gypsum-containing precipitates. It consisted of irregular shaped greenish lumps which were subsequently identified by x-ray diffraction to be magnesium hydroxide or brucite (Figure 3-B in Appendix B). This is consistent with the relatively high magnesium assay (16.8% Mg) given in Table 5-12.

The morphology of Precipitate No. 12, the first-stage precipitate from the Key Lake waste treatment circuit simulation test, was the same as the first eleven precipitates produced by neutralization of Key Lake raffinate above. Hence it can be concluded that the precipitates being formed in the actual waste treatment circuit at Key Lake are the same as the precipitates evaluated in this study.

X-ray diffraction patterns of Precipitates No. 1 to No. 12 showed the presence of only gypsum. The X-ray diffraction chart for Precipitate No. 1 is shown in Figure 4 of Appendix B. The charts for Precipitates No. 2 to No. 12 were the same as that shown for Precipitate No. 1. The X-ray diffraction pattern of Precipitate No. 13, shown in Figure 5 of Appendix B, indicated that it was magnesium hydroxide in the presence of gypsum.

6.3 CHEMICAL CHARACTERIZATION

Examination of the low micron-size particles in the precipitates by a transmission electron microscope (TEM) equipped with an EDAX analysis system (Figure 3-D of Appendix B) showed that the fine-grained aggregates contain iron, nickel, arsenic, aluminum, silica, sulphur and calcium, with iron, silica and aluminum content being variable. The TEM results for Precipitates No. 1 and No. 4 are presented in Figure 6 of Appendix B.

Electron microprobe analysis (EM) of the precipitates basically gave the same results as the TEM analysis of fine-grained material. The EM-ADAX results for Precipitate No. 2 are presented in Figure 8-A of Appendix B. Quantitative analyses could not be obtained by the TEM or EM analysis due to sample preparation difficulties and due to the sub-micron grain size of the precipitates.

In order to obtain a better interpretation of the chemical make-up of the precipitate constituents, Precipitates No. 1, 4, 5 and 7 were repeatedly dispersed in water thereby dissolving the contained gypsum and producing precipitate "residues" for analysis and examination. Analyses of the four precipitate residues produced, labelled as No. 1W, 4W, 5W and 7W, are given in Table 6-2.

X-ray diffraction of these four residues (shown in Figure 7 of Appendix B) showed no diffraction peaks indicating that they are amorphous. This confirms the fact that no X-ray diffraction peaks other than gypsum were obtained in Precipitates No. 1 to No. 12.

An SEM examination of the four concentrates (Figures 3-E and 3-F of Appendix B) concluded that these concentrated residues of the precipitates are made up of sub-micron size particles whose morphology and size are very similar to the aggregate of fine-grained crystals observed in the precipitates and in the pisoliths.

Based on these similarities it can be tentatively concluded that the yellow-brown amorphous residues, the aggregates of crystals scattered throughout the

TABLE 6-2
ANALYSIS OF PRECIPITATE "RESIDUES" (%)

	Precipitate "Residue"			
	1W**	4W	5W	7W
Elemental				
Al	8.7	4.9	3.4	0.1
Si	3.5	1.9	2.2	0.7
S	-	-	0.41	-
Ca	0.1	1.8	2.6	0.1
Fe	12.1	12.4	7.5	17.1
Ni	2.2	17.6	11.4	29.6
As	19.1	9.7	7.1	0.4
V	0.4	0.2	0.1	0.01
Zn	0.2	0.4	0.3	0.6
Co	0.04	0.2	0.2	0.5
Cu	0.4	0.3	0.2	0.05
Y	0.3	0.2	0.2	0.1
LOI*	30.0	30.0	42.0	35.0
Oxide Form				
Al_2O_3	16.4	9.3	6.4	0.2
SiO_2	7.5	4.1	4.7	1.5
SO_4	-	-	1.2	-
CaO	0.1	2.5	3.6	0.1
Fe_2O_3	17.3	17.7	10.8	24.5
NiO	2.7	22.4	14.5	37.7
As_2O_3	25.2	12.8	9.4	0.5
V_2O_5	0.7	0.4	0.2	0.02
ZnO	0.3	0.5	0.4	0.8
Co_3O_4	0.1	0.3	0.3	0.7
CuO	0.5	0.3	0.3	0.1
Y_2O_3	0.3	0.3	0.2	0.2
LOI*	30.0	30.0	42.0	35.0
Total %	101.1	100.7	94.0	101.3

* LOI - Loss on Ignition

** W - washed

precipitates, and the material comprising the shells of pisoliths are the same substance.

The EM-ADAX analysis of the four residues, illustrated for sample IW in Figure 8-B of Appendix B, indicated that the yellow-brown amorphous material and the shells of the pisoliths can contain relatively large concentrations of iron, nickel and arsenic and generally lower concentrations of silica and aluminum.

Chemical analysis of the water-leached amorphous material, expressed as oxides, showed that it can contain up to 37.7% NiO, 25.2% As_2O_3 and 24.5% Fe_2O_3 with lower concentrations of Al_2O_3 and SiO_2. Ca, S, V, Zn, Co, Cu, Y are only minor constituents of the amorphous material. The fact that the oxides total very close to 100% and that there is a high loss on ignition for the residues suggests that the concentrates are a mixture of oxides and hydroxides. Analysis of the leach water for one of the samples (No 5) indicated that the amorphous material had a low solubility in water, suggesting that the composition of the insoluble residues are representative of the amphorous material in the original samples.

Selected precipitates were submitted to Raman microprobe examination along with six reference standards that were prepared as described in Appendix C. The reference standards were made up from synthetic solutions in attempt to produce the six compounds listed in Table 6-3. The XRD charts for these synthetic standards are shown in Figures 9 and 10 of Appendix B. Only Standard R-4 (magnesium arsenate) showed a reasonable crystallinity with the other five standards being amorphous.

The Raman spectra for two of the precipitates, No. 1 and No. 5, are shown in Figures 11 and 12 of Appendix B. The Raman spectra for the six reference standards are given in Figure 13 of Appendix B.

The only conclusive result of the Raman investigation was that the yellow-brown amorphous material and the shells of the pisoliths produced a weak

TABLE 6-3
REFERENCE STANDARDS FOR RAMAN MICROPROBE ANALYSIS

Standard No.	Chemical Compound
R-1	Ferric Arsenate (pH 5)
R-2	Calcium Arsenate (pH 9)
R-3	Nickel Arsenate (pH 9)
R-4	Magnesium Arsenate (pH 9)
R-5	Nickel Hydroxide (pH 9)
R-6	Calcium Arsenate (pH 11)

Raman band which is in the same position as the single weak Raman band obtained for the ferric arsenate reference material (324 to 326 cm^{-1}). This would therefore suggest, or perhaps confirm, that the precipitates are amorphous mixtures of hydrous oxides with only minor amounts of ferric arsenate being present as a precipitate.

7.0 GEOCHEMICAL MODEL

7.1 GENERAL

As described in Section 3.0 Key Lake ore deposits contain substantial quantities of arsenic and nickel minerals. During the milling process a portion of these minerals tend to undergo oxidation and partially dissolve in the uranium leaching circuit. Dissolved arsenides were believed to oxidize rapidly to arsenates. During waste treatment of liquid effluents by precipitation with lime at elevated pH values, the arsenic and nickel were believed to be deposited in the tailings as arsenate complexes and nickel hydroxysulphate complexes.

Arsenic

Analysis of monitored arsenic concentrations in tailings influent, in tailings porewater, and in leachates at Key Lake (Knight and Piesold Ltd., 1985 and Sherritt Gordon, 1979) indicated that solubility of calcium arsenate ($Ca_3(AsO_4)_2$) controls the liquid phase concentrations at pH values of pH 10 to pH 12. This implies that soluble arsenic is deposited in the tailings as calcium arsenate. Arsenic concentrations of 0.23 mg/L As (pH 12) to 1.62 mg/L As (pH 10), predicted from $Ca_3(AsO_4)_2$ solubility equilibria, compared well with measured concentrations of 0.26 to 2.2 mg/L As. Below pH 10, however, the measured concentrations were significantly less than predicted values. At near pH neutrality (pH 7) for example, measured porewater arsenic concentrations were 2.0-2.2 mg/L As in comparison to predicted values in excess of 100 mg/L As.

Two hypotheses have been previously suggested as geochemical controls for arsenic in the Key Lake tailings. The first involves the incongruent solution of the calcium arsenate and reprecipitation of the dissolved species as a second solid phase. This has been tentatively proposed by SENES Consultants Limited (Knight and Piesold Ltd., 1985) to explain an apparent plateau in dissolved arsenic (V) concentrations in the tailings porewater between pH 10 and pH 7 but there is a lack of mineralogical data to support this proposal. The second hypotheses by Beak Consultants Limited (1986) is that arsenic solubility is controlled by adsorption onto aluminum and ferric hydroxide solids.

Other possibilities for solubility control also exist and these include the potential that arsenate species are occluded by a gypsum (or other host mineral) matrix. In this case, neither calcium arsenate solubility nor adsorption equilibria are the controlling factors. Rather, the concentrations in the porewater would depend on the rate of solution of the host mineral.

All of the above have been proposed on the basis of limited data on the mineralogical nature of arsenic precipitate and in fact no specific arsenic precipitates had been identified. It was also based upon the belief that arsenic (V) was the dominant (if not only) valency and that little to no arsenic (III) could have remained after milling under such strong oxidizing conditions.

This current study was therefore directed at detecting the primary arsenic species and determining a reasonable mechanism for solubility control.

Nickel

The solution chemistry of nickel minerals is equally complex. In neutralized raffinates at Key Lake (Knight and Piesold Ltd., 1985), partly dissolved and partially oxidized nickel minerals (millerite, nickel arsenides, etc.) reprecipitate as nickel hydroxide ($Ni(OH)_2$). It has been shown that solubility and complexation equilibria control dissolved nickel into the tailings porewater down to pH 8. Below pH 8 $Ni(OH)_2^{(s)}$ is unstable and a new solid phase may form. As in the case of arsenic solids, the solid phase controlling the concentration of nickel in the porewater was unknown.

Beak (1986) also reviewed the geochemical data for Key Lake tailings and suggest that evidence exists for both simple nickel hydroxide and nickel ferrite ($NiFe_2O_4$) control for nickel solubility.

As with arsenic, no nickel precipitates were identified in previous mineralogical examination studies. The object of this study was then to identify mineral precipitates of nickel and to determine a rational geochemical mechanism for nickel solubility control.

Since the mineralogical examinations reported in this study have not been successful in determining the exact chemical nature of arsenic and nickel precipitates formed in the Key Lake tailings it is necessary to first review the basic principles of nickel and arsenic chemistry to arrive at a tentative geochemical model for these two species. An assessment and interpretation of the chemical analysis results from the study, based on nickel and arsenic equilibrium data, can then provide some tentative conclusions with respect to the long-term behaviour of nickel and arsenic in uranium tailings.

7.2 BASIC PRINCIPLES AND DATA

7.2.1 Equilibrium Data

Equilibrium data for arsenic compounds of interest are very limited. Data are available for arsenic acid and selected metal arsenates but data needs to be calculated from available thermodynamic data for many of the arsenic species of interest. These data along with the data for nickel compounds (as summarized by Beak (1986)) are provided in Table 7-1.

7.2.2 Arsenic Speciation

Original geochemical models assumed that arsenic in raffinate was present as As(V) but an arsenic speciation assay of the raffinate used in the testwork showed an As(III)/As(V) ratio of 7 to 1. This unexpected presence of significant amounts of arsenite in the raffinate has previously been reported (Neven et al, 1985) with the As(III)/As(V) ratio expected to vary depending on the mill circuit chemistry.

When considering solubility data, the presence of As(III) only complicates the assesssment of low arsenic solubility in the pH 5-10 range. The low solubilities do not support the presence of arsenites.

A thermodynamically supportable reaction indicates that the As(III)/As(V) ratio in a ferric iron system is very pH dependent. As pH is increased, arsenite is oxidized and ferric iron is reduced as shown below.

$$H_3AsO_3 + H_2O + 2\ Fe^{3+} \text{--->} H_3AsO_4 + 2\ H^+\ 2\ Fe^{2+}$$

$$\frac{[H_3AsO_4]}{[H_3AsO_3]} = K \left[\frac{Fe^{3+}}{Fe^{2+}}\right]^2 10^{-2pH}$$

This reaction could explain why iron stays in solution at pH levels of 5.0 during the testwork since iron has been partly reduced to the ferrous state. Given this premise is correct then the original hypotheses, that arsenate is the species precipitated and is the primary control on arsenic solubility, is valid.

TABLE 7-1
SOLUBILITY AND COMPLEXATION EQUILIBRIA

Arsenic Species

Reaction	log Keq (2)
$2AsO^{+} + H_2O = As_2O_{3(s)} + 2H^{+}$	- 2.04
$As_2O_{3(s)} + H_2O = 2HAsO_2$	- 1.36
$As_2O_{3(s)} + H_2O = 2AsO_2^{-} + 2H^{+}$	-19.78
$As_2O_{5(s)} + 3H_2O = 2H_3AsO_4$	- 9.48
$As_2O_{5(s)} + 3H_2O = 2H_2AsO_4^{-} + 2H^{+}$	- 2.30
$As_2O_{5(s)} + 3H_2O = 2HAsO_4^{2-} + 4H^{+}$	-12.24
$As_2O_{5(s)} + 3H_2O = 2AsO_3^{3-} + 6H^{+}$	-37.18
$Ca_3(AsO_4)_{2(s)} = 3Ca^{2+} + 2AsO_4^{3-}$	-18.17
$Mg_3(AsO_4)_{2(s)} = 3Mg^{2+} + 2AsO_4^{3-}$	-19.68
$CaHAsO_4(s) = Ca^{2+} + HAsO_4^{2-}$ (3)	- 3.34
$Ca_3(AsO_4)_2 \cdot Ca(OH)_2(s) = 4Ca^{2+} + 2AsO_4^{3-} + 2OH^{-}$ (3)	-26.24
$FeAsO_4(s) = Fe^{3+} + AsO_4^{3-}$ (3)	-20.26
$AlAsO_4(s) = Al^{3+} + AsO_4^{3-}$ (3)	-15.12
$Fe_3(AsO_4)_2(s) = 3Fe^{2+} + 2AsO_4^{3-}$ (3)	-40.85

Nickel Species

Reaction	log Keq (1)
$Ni^{2+} + H_2O = NiOH^{+} + H^{+}$	- 9.86
$Ni^{2+} + 2H_2O = Ni(OH)_2^{o} + 2H^{+}$	-20.28
$Ni^{2+} + 3H_2O = Ni(OH)_3^{-} + 3H^{+}$	-29.05
$Ni^{2+} + 4H_2O = Ni(OH)_4^{2-} + 4H^{+}$	-44.0
$4Ni^{2+} + 4H_2O = Ni_4(OH)_4^{4+} + 4H^{+}$	-27.71
$Ni^{2+} + Cl^{-} = NiCl^{+}$	+ 0.747
$Ni^{2+} + SO^{2-} = NiSO_4^{o}$	+ 2.31
$Ni^{2+} + CO_3^{2-} = NiCO_3^{o}$	+ 5.35
$Ni^{2+} + HCO_3^{-} = NiHCO^{+}$	+ 2.2
$Ni(OH)_2$ (alpha) $+ 2H^{+} = Ni^{2+} + 2H_2O$	+15.03
$Ni(OH)_2$ (beta) $+ 2H^{+} = Ni^{2+} + 2H_2O$	+10.81
$NiFe_2O_4(s) + 2H^{+} + 2H_2O = Fe(OH)_3(am) + Ni^{2+}$	+ 0.105
$NiFe_2O_4(s) + 2H^{+} = FeOOH(s) + Ni^{2+}$	+ 9.64
$NiS(s) = Ni^{2+} + S^{2-}$	-22.9

Notes

1. From Beak 1986
2. From Faust 1981
3. Calculated values

7.2.3 Ionic Strength

The ionic strength of raffinate solutions is extremely important with respect to solubility and ion activity. The ionic strength is variable over the range of experiments performed. It has been calculated as shown on Table 7-2 along with the respective activity coefficients for the ion species.

With the calculated ionic strength, the activity coefficients, shown on Table 7-2, were then derived by the modified Davies expression (Stumm and Morgan, 1981):

$$\log f = 1.82 \times 10^{6} \, (ET)^{-3/2} Z^{2} \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right)$$

$$= 0.5 \, Z^{2} \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right)$$

where:

f = activity coefficient

E = dielectric constant for water

T = Absolute temperature (°K).

I = ionic strength (M)

Z = ion charge

TABLE 7-2
IONIC STRENGTH AND ACTIVITY COEFFICIENTS VS. PH FOR LIMED RAFFINATE

pH	Ionic Strength (moles/L)	Activity Coefficient for Ion Charge			
		0	1	2	3
2	0.5	1	0.74	0.3	0.06
5	0.2	1	0.75	0.32	0.08
6	0.14	1	0.77	0.35	0.09
7	0.10	1	0.79	0.38	0.11
8	0.08	1	0.80	0.4	0.13
9	0.06	1	0.81	0.44	0.16
11	0.04	1	0.84	0.5	0.21

7.3 SOLID/LIQUID ANALYSIS

7.3.1 Solids Chemistry/Mineralogy

Very little direct evidence as to the nature of the arsenic or nickel species was forthcoming from the mineralogical examination of the limed raffinate precipitates. However, there is a substantial amount of data that can be obtained from the chemical composition of the precipitates. By knowing the major chemical species that are likely to be present, molar balances can be calculated to provide a tentative mineralogical composition. For phosphate concentrations in solid phases, concentrations have been estimated from the liquid phase data. The primary raw data sources are listed in Tables 5-3, 5-5 and 5-6 of Section 5.3.2. The molar ratios for the precipitates are provided in Table 7-3. The mineral composition of each precipitate is discussed below.

pH 2 - Gypsum Removal Precipitate

Gypsum accounts for 80 percent of the precipitate removed at pH 2. The other primary components in order of occurrence are arsenic, iron, phosphate, aluminum, silica and magnesium.

The molar ratios from Table 7-3 indicate that iron and aluminum balance arsenic and phosphate and these compounds are believed to be present as $FePO_4$, $FeAsO_4$, $AlPO_4$, and $AlAsO_4$. Small amounts of $MgSO_4$ and silicate minerals (Ca, Mg, Al etc.) are also present.

pH 5.0 Precipitate

The primary mineral present is again calcium suphate. Arsenic may be precipitated by aluminum or more likely a combination of aluminum and iron. The residual iron and aluminum will be precipitated as hydroxides, phosphates and possibly clay minerals. The precipitation of nickel begins at pH 5 and is likely present as a nickel hydroxide/sulphate complex.

TABLE 7-3

MOLE RATIOS OF LIMED RAFFINATE PRECIPITATES AT VARIOUS PH VALUES

pH	Mg	SO_4	SiO_2	Al	As	Cu	Fe	Ni	Ca	PO_4
2.0	.00601	.46097	.00435	.00968	.02370	.00023	.02057	.00890	.46121	.00440
5.0	.00781	.32094	.03972	.11728	.09050	.00000	.06314	.02310	.31580	.02170
6.0	.01046	.32590	.03298	.08450	.06555	.00000	.07537	.06125	.32819	.01579
7.0	.01903	.29166	.02638	.06986	.05032	.00000	.05830	.08758	.38479	.01209
8.0	.02766	.28004	.02529	.06151	.04663	.00000	.05474	.07886	.41405	.01122
9.0	.05464	.28521	.02225	.06462	.04876	.00000	.05649	.08345	.37287	.01171
11.0	.05090	.28983	.02368	.05569	.04483	.00000	.05223	.07529	.39695	.01061

pH 6-9 Precipitates

No major differences in the mineralogical composition of the arsenic precipitates was noticed in this pH range.

Nickel precipitation is essentially complete by pH 9 which is consistent with $Ni(OH)_2$ precipitation. There is also some possibility that nickel may combine with iron and precipitate as a nickel ferrite (Beak, 1986), however, it would appear that there is insufficient iron present for this mechanism to play a major role in precipitation. Also iron has been removed from solution before nickel precipitates.

pH 11 Precipitate

At pH 11 it is possible that calcium arsenate is also formed in combination with iron and aluminum arsenate. However, examination of the precipitates concluded that the amorphous material precipitated at all pH values is essentially the same.

Summary

Based upon the mineralogical testwork and the chemical analysis it is believed that arsenic is present as aluminum and iron arsenates in equilibrium with their respective metal hydroxides. Potential exists for small amounts of calcium arsenate to precipitate at elevated pH levels. Nickel appears to precipitate as an hydroxide or hydroxysulphate complex.

7.3.2 Liquid Chemistry

The molar concentrations of arsenic and nickel in combination with selected metals and anions are plotted versus pH on Figures 7-1, 7-2, and 7-3, and are then summarized in Table 7-4. Concentrations are provided for the residual concentrations in filtered raffinate after pH adjustment with lime and chemical precipitation.

These data support the conclusions reached from reviewing the solids chemistry data. In general, arsenic removal is coincidental with iron and aluminum precipitation. Nickel precipitation is independent of other metals or anion removal.

FIGURE 7-1

LIMED RAFFINATE QUALITY

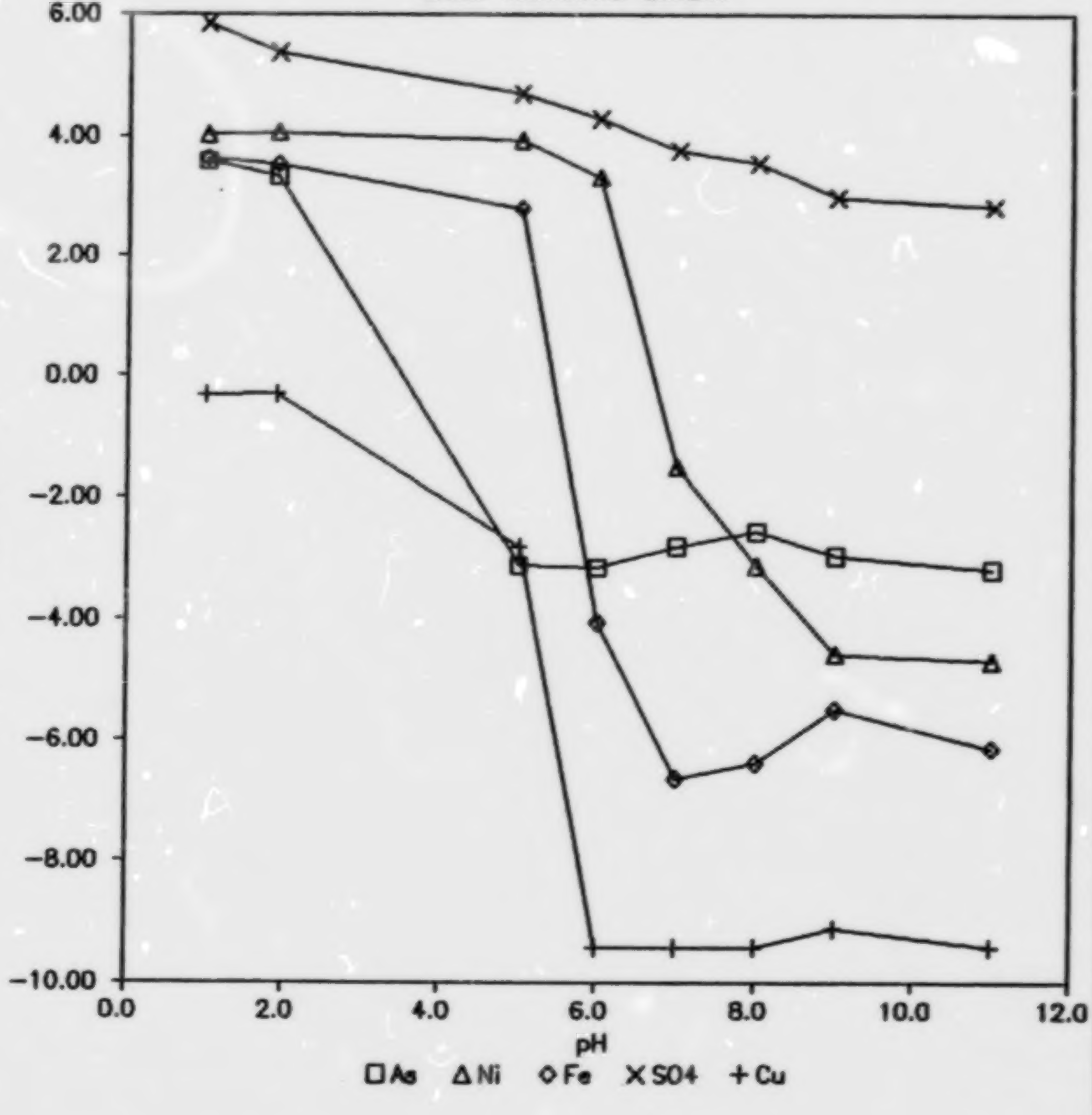


FIGURE 7-2
LIMED RAFFINATE QUALITY

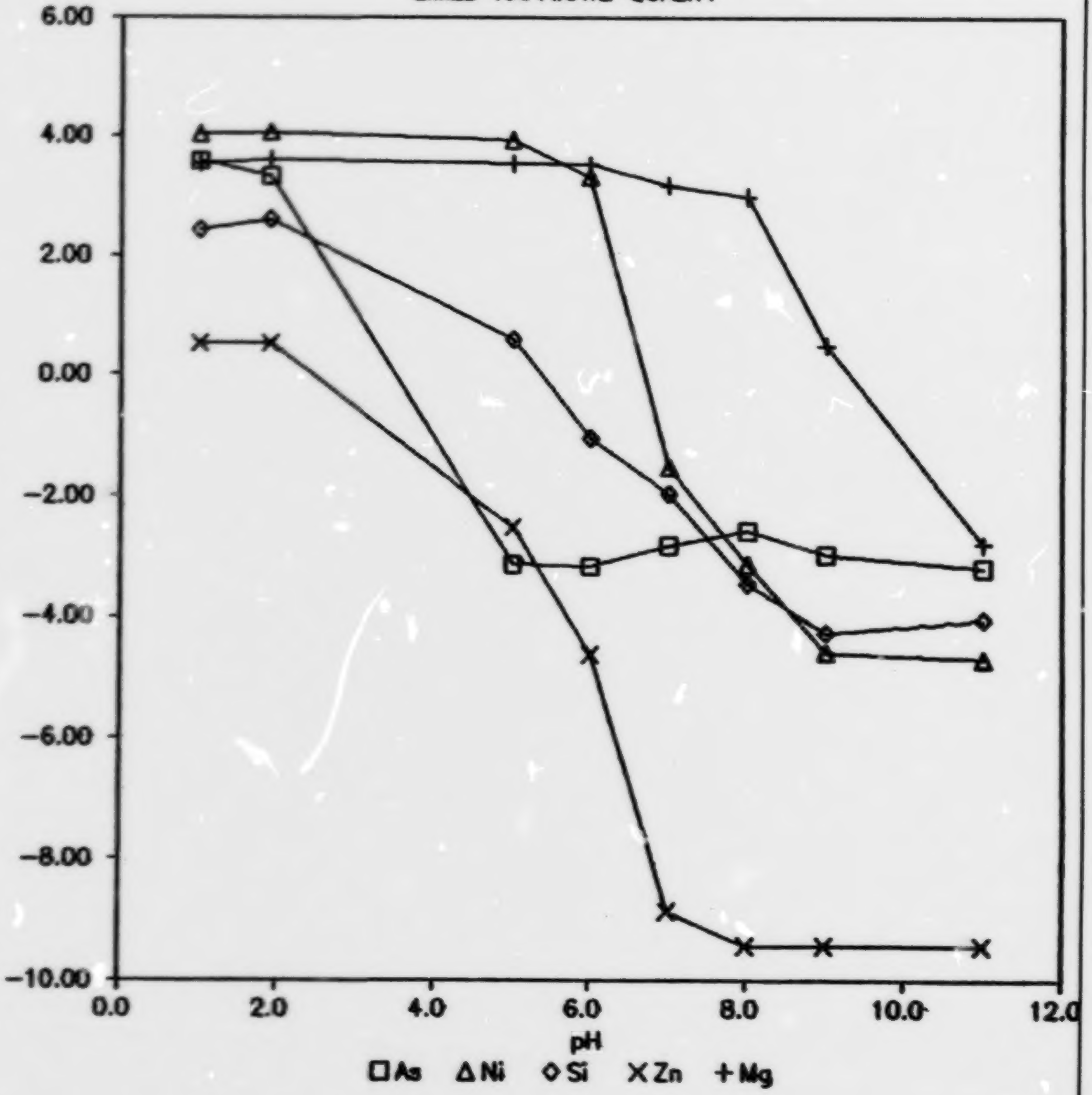


FIGURE 7-3
LIMED RAFFINATE QUALITY

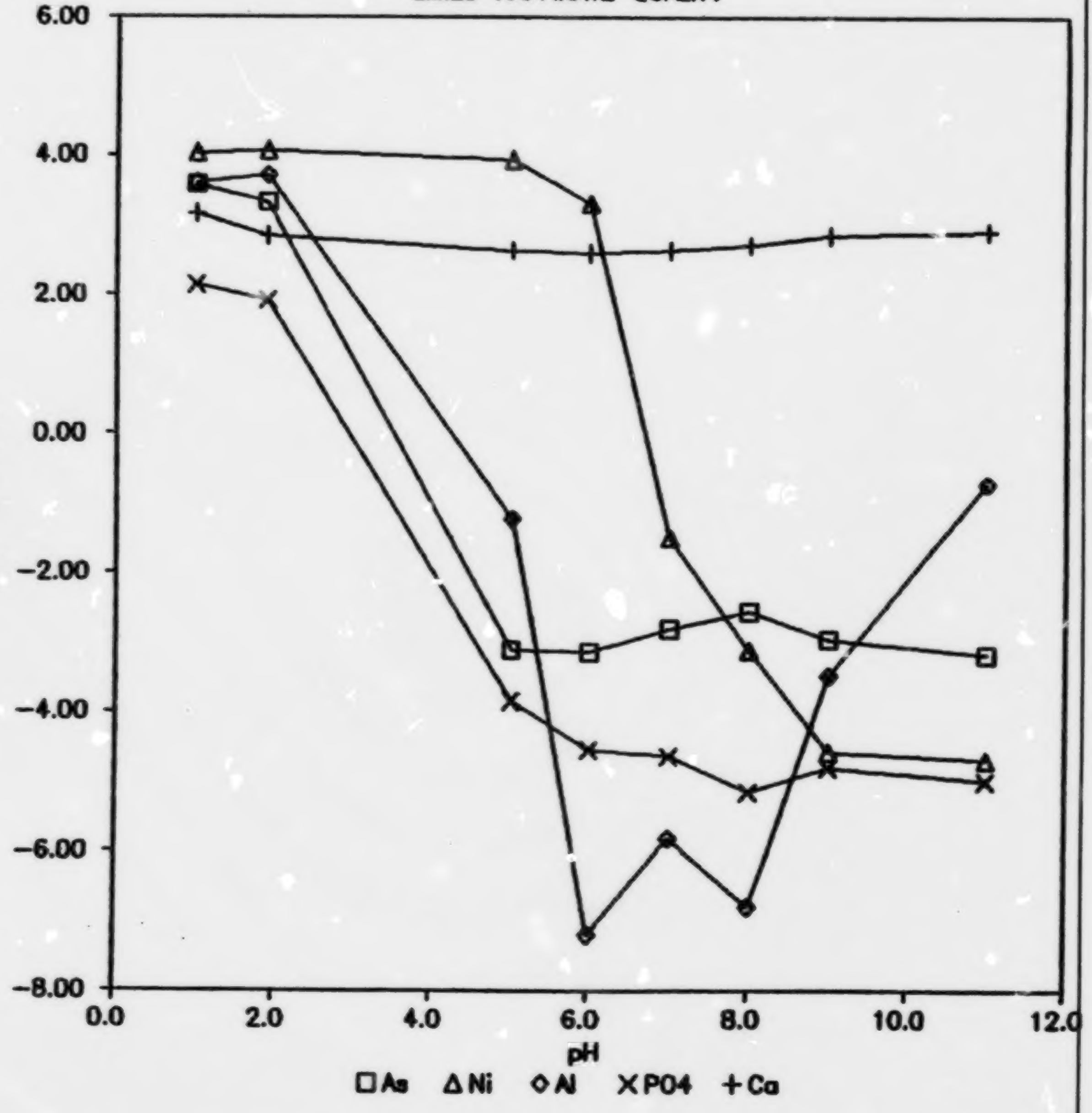


TABLE 7-4

MOLAR CONCENTRATION OF SOLUBLE CONSTITUENTS IN LIMED RAFFINATE

(M MOLES/L)

pH	Ca	Ni	As	Mg	Fe	Al
1	23.703	56.218	36.038	34.551	37.603	37.062
2	17.216	57.922	28.029	36.607	34.022	40.769
5	13.972	51.107	0.044	34.551	16.295	0.285
6	13.473	27.257	0.043	33.728	0.017	0.001
7	14.222	0.221	0.060	23.857	0.001	0.003
8	15.220	0.044	0.077	19.743	0.002	0.001
9	17.465	0.010	0.052	1.645	0.004	0.031
11	18.463	0.009	0.041	0.062	0.002	0.489

pH	Cu	Pb	Si	Zn	SO_4	PO_4
1	0.724	0.001	11.394	1.683	45.616	8.529
2	0.740	0.0001	13.530	1.683	16.528	6.739
5	0.060	0.001	1.816	0.081	10.346	0.021
6	0.0001	0.0001	0.356	0.010	72.662	0.011
7	0.0001	0.0001	0.142	0.0001	42.993	0.010
8	0.0001	0.0001	0.032	0.0001	34.665	0.006
9	0.0001	0.0001	0.014	0.0001	19.779	0.008
11	0.0001	0.0001	0.018	0.0001	16.968	0.007

7.4 GEOCHEMICAL MODEL FOR ARSENIC PRECIPITATION

7.4.1 General

Based upon the experimental data and lack of mineralogical proof for a stable arsenic solid phase, it is hypothesized that four primary precipitation reactions occur. These all include the precipitation of a metal arsenate in combination with the corresponding metal hydroxide complex. Increased metal hydroxide levels appear to improve the stability of the complexes. The primary metal arsenate species include $AlAsO_4$, $FeAsO_4$, $Fe_3(AsO_4)_2$, and $Ca_3(AsO_4)_2$. The geochemical models for each of these arsenates is reviewed below.

7.4.2 Aluminum Arsenate Precipitation

To date, the most extensive study of metal arsenate precipitation has been reported by Chukhlansev (1956). This author has compiled an extensive thermodynamic database concerning the stability of various metal arsenates and this database is regarded as authorative for estimating the solubility products of the metal arsenates. It appears that the only stable solid is the simple salt, aluminum arsenate ($AlAsO_4$). The equilibrium activities of the aluminum ion (Al^{3+}) and the trivalent arsenate ($AsO_4{}^{3-}$) are related by the solubility product (K_{so}) as follows:

$$AlAsO_4(s) \text{ ---> } Al^{3+} + AsO_4{}^{3-}$$
$$K_{so} = (Al^{3+})\ (AsO_4{}^{3-})$$

where:

K_{so} = solubility product

(Al^{3+}); $(AsO_4{}^{3-})$ = equilibrium activities of the aluminum and the arsenate ions in solution.

To calculate the concentration of total dissolved arsenate $[As]_T$ as a function of pH, it is necessary to determine the equilibria of various dissolved arsenate species in solution. The relevant equilibrium expressions have been compiled by Faust and Aly (1981) as follows:

H_3AsO_4 ---> $H_2AsO_4^-$ + H^+ log K = -3.60
$H_2AsO_4^-$ ---> $HAsO_4^{2-}$ + H^+ log K = -7.26
$HAsO_4^{2-}$ ---> AsO_4^{3-} + H^+ log K = -12.47.

Using the above equilibrium constants, the total activity of dissolved arsenate in solution becomes:

$$\{As\}_T = \{AsO_4^{3-}\}\ (1 + 10^{12.47-pH} + 10^{19.73-2pH} + 10^{23.33-3pH})$$

The dissociation constants shown in the above expression refer to low ionic strength (I=0) solutions. In the Key Lake raffinate, however, the ionic strength of the solution is not negligible. In pH adjusted raffinate solutions, the ionic strength of the raffinate is estimated to be about 0.2M. Calculating activity coefficients of 0.75, 0.35, and 0.08 for monovalent, divalent, and trivalent arsenic(V) ions, respectively, the mole fraction of AsO_4^{3-} in the solution becomes:

$$y = \frac{[AsO_4^{3-}]}{[As]_T} = \frac{1}{1 + 10^{11.84-pH} + 10^{18.73-2pH} + 10^{22.08-3pH}}$$

Using the above mole fraction, the activity of the AsO_4^{3-} species can be conveniently expressed in terms of the total dissolved arsenic(V) concentration in the following manner:

$$[AsO_4^{3-}] = f_3\ y\ [As]_T = \frac{f_3[As]_T}{1 + 10^{11.84-pH} + 10^{18.73-2pH} + 10^{22.08-3pH}}$$

where f_3 is the activity coefficient for the triply charged anion.

The next step is the speciation of dissolved aluminum in equilibrium with the solid phase, $AlAsO_4(s)$. The relevant complexation reactions of dissolved aluminum are as follows (Stumm and Morgan, 1981):

Al^{3+} + H_2O ---> $Al(OH)^{2+}$ + H^+ log K = -4.97
Al^{3+} + $2H_2O$ ---> $Al(OH)_2^+$ + $2H^+$ log K = -9.30
Al^{3+} + $3H_2O$ ---> $Al(OH)_3$ + $3H^+$ log K = -15.0
Al^{3+} + $4H_2O$ ---> $Al(OH)_4^-$ + $4H^+$ log K = -23.5
Al^{3+} + SO_4^{2-} ---> $AlSO_4^+$ log K = 3.20

As in the case of arsenate, the above equilibrium constants refer to low ionic strength solutions. Adjustment of the equilibrium constants to an ionic strength of 0.2M gives the following relationship for the mole fraction of trivalent aluminum ion (Al^{3+}) in solution:

$$(y)Al^{3+} = \frac{[Al^{3+}]}{[Al]_T} = \frac{1}{1+10^{pH-5.61}+10^{2pH-10.27}+10^{3pH-16.10}+10^{4pH-24.47}+10^{1.61}[SO_4^{2-}]}$$

where:

$[Al^{3+}]$ = concentration of Al^{3+} (M)

$[Al]_T$ = total dissolved aluminum concentration (M)

$[SO_4^{2-}]$ = sulphate concentration (M).

The activity of aluminum ion can be expressed as the combination of total dissolved aluminum $[Al]_T$ and the activity coefficient of the trivalent aluminum ion, f_3:

$$[Al^{3+}] = \frac{f_3[Al]_T}{1+10^{pH-5.61}+10^{2pH-10.27}+10^{3pH-16.10}+10^{4pH-24.47}+10^{1.61}[SO_4^{2-}]}$$

The solubility product K_{so} is, of course, the product of the arsenate (AsO_4^{3-}) and aluminum (Al^{3+}) activities.

However, the evaluation of the concentrations of the respective constituents is subject to certain constraints. At low pH values, where aluminum cannot precipitate as amorphous aluminum hydroxide ($Al(OH)_3(am)$), the stoichiometric constraints are as follows:

$$[As]_{T,0} = [As]_T + [As]_p$$
$$[Al]_{T,0} = [Al]_T + [Al]_p$$

where:

$[As]_{T,0}$ = total initial dissolved arsenic(V) concentration in the raffinate pH 2

$[As]_T$ = total dissolved arsenic(V) concentration after pH adjustment (M)

$[As]_p$ = precipitated arsenic(V) concentration (M)

$[Al]_{T,0}$ = total initial dissolved aluminum concentration in the raffinate, pH 2 (M)

$[Al]_T$ = total dissolved aluminum concentration after pH adjustment (M)

$[Al]_p$ = precipitated aluminum concentration (M).

Since the molar ratio of precipitated arsenic(V) to aluminum is 1:1, the total aluminum in solution after pH adjustment can be expressed as the function of total arsenate $(As)_T$ as follows:

$$[Al]_T = [Al]_{T,0} - ([As]_{T,0} - [As]_T) = [As]_T + [Al]_{T,0} - [As]_{T,0}$$

Combination of the above equations with the solubility product expression yields the following equations to total arsenate in solutions:

$$[As]T = \frac{[As]_{T,0} - [Al]_{T,0} + (([As]_{T,0} - [Al]_{T,0})^2 - 4K)^{1/2}}{2}$$

where:

$$K = \frac{Kso(1+10^{11.84-pH}+10^{18.73-2pH}+10^{22.08-3pH}) \ldots(1+10^{pH-5.61}+10^{2pH-10.27}+10^{3pH-16.10}+10^{4pH-24.47}+10^{1.61}[SO_4{}^{2-}]}{f_3{}^2}$$

where:

Kso = solubility product of $AlAsO_4$

f_3 = activity coefficients of trivalent ions.

At some pH value, however, aluminum is expected to precipitate as $Al(OH)_3$. The activity of Al^{3+} in equilibrium with amorphous $Al(OH)_3$ is given by the following equilibria:

$$Al(OH)_3(s) + 3H^+ \text{--->} Al^{3+} + 3H_2O \qquad \log Kso = 10.8$$

It can be shown, that aluminum hydroxide becomes stable at pH values greater than pH 4.9. At pH values greater than pH 4.9, the relevant expession to calculate the total dissolved arsenate becomes:

$$[As]_T = \frac{K_{so} (1 + 10^{11.84-pH} + 10^{18.73-2pH} + 10^{22.08-3pH}),}{f_3\ 10^{10.8-3pH}}$$

The concentrations of total dissolved arsenate after pH adjustment of the raffinate solution were evaluated using the following initial conditions. The concentrations are summarized on Table 7-5.

$[As]_{T,0} = 2.8 \times 10^{-2}$ M
$[Al]_{T,0} = 4.8 \times 10^{-2}$ M
Initial pH = 2.0

The solubility product (Kso) was estimated from precipitation studies performed during the course of this study. The adjustment to pH 5 of synthetic arsenate solutions gave a concentration of 49 mg/L total arsenate at pH 5. Using this value, the solubility product is estimated to be Kso = $10^{-17.2}$). Although this solubility product is substantially lower then the corresponding value calculated from the thermodynamic database (Kso = $10^{-15.2}$), experimental data on solid composition in this study strongly suggest that at least some arsenate precipitates as aluminum arsenate.

Aluminum may also precipitate some arsenites. However, the solubility of aluminum arsenites is substantially greater than those of arsenates, thus they are not considered as being stable in the raffinate solution.

7.4.3 Iron(III) - Arsenic(V) Precipitation

The precipitation of arsenates by ferric ion has been studied by several workers (Krause and Ettel, 1985; Tozawa and Nishimura, 1984). These studies have shown that arsenate can be removed from hydrometallurgical process solutions by the addition of ferric ion in great excess of the required stoichiometric ratio as $FeAsO_4$ and adjusting the pH from pH 4 to pH 5 (Krause

TABLE 7-5
PREDICTED ARSENIC CONCENTRATIONS FOR $AlAsO_4$ PRECIPITATION

	As (mg/L)	
pH	Model Prediction	Raffinate Concentration
2	> 2100	2100
4	847	--
4.5	111	--
5	52*	3.3
5.5	167	--
6	570	3.2

* when arsenic was precipitated from a $CaSO_4$ solution with aluminum alone, the arsenic concentration was 49 mg/L. This agrees with the model prediction for $AlAsO_4$ precipitation.

and Ettel, 1985). This process has been reported to give rise to the formation of thermodynamically stable basic ferric hydroxides. Robins (1985) has reviewed the thermodynamics and the stability of ferric arsenate compounds. This author has stated that although the inorganic chemistry of metal-arsenic compounds is yet to be understood completely, ferric arsenates lack sufficient stability for long-term disposal in dumps or ponds.

The theoretical precipitation and solubility of arsenic as ferric arsenate from Key Lake tailings has been evaluated. The purpose of the evaluation was to determine the significance of arsenic precipitation as iron(III) arsenate in the raffinate after pH adjustment. The calculations for modelling precipitate formation and solubility equilibria were performed with the following initial concentrations in solution:

Constituent	Concentration (M)
Total Iron (Fe^{III})	3.4×10^{-2}
Total Arsenic(V)	2.8×10^{-2}
Total Sulphate	2.2×10^{-1}
Total Calcium	1.7×10^{-2}
pH	2.0

The above concentrations are essentially identical with concentrations observed in the Key Lake raffinate at pH 2.

The equilibrium expressions for estimating arsenic precipitation involved the speciation of dissolved arsenic (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}), iron (Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $FeSO_4^+$), sulphate (HSO_4^-, SO_4^{2-}, $FeSO_4^+$, $CaSO_4$ (aq)) and calcium (Ca^{2+}, $CaSO_4$ (aq)). The relevant equilibria are summarized in Table 7.1.

Since the calculations were performed for a closed system, as were the experimental studies, the concentrations of total dissolved iron and total dissolved arsenic were subject to stoichiometric balance constraints. Arsenic precipitates as $FeASO_4$, while iron precipitation included both ferric arsenate and amorphous ferric hydroxide ($Fe(OH)_3(am)$), depending on the pH.

The modelling results for the Key Lake raffinate are shown in Figure 7.4 of Section 7.4.6. In general, the ferric arsenate precipitation/dissolution profile is similar to the experimental results of Krause and Ettel (1985). Most of the arsenate (73%) is expected to precipitate between pH 2 to pH 3. Minimum arsenate solubility occurs at about pH 3.5. Dissolved ferric ion would start precipitating as amorphous ferric hydroxide at pH 2.9. It is evident, however, that even the minimum solubility of 120 mg/L arsenic is several orders of magnitude above the concentrations observed in the pH adjusted raffinate. Furthermore, precipitated ferric arsenate appears to be unstable above pH 4 as iron would precipitate preferentially as ferric hydroxide. The lack of stability of iron(III) arsenates above pH 4 has been observed by Robins (1985). It has been suggested (Beak, 1986) that adsorption of dissolved arsenate on metal hydroxides is a major mechanism controlling arsenate mobility at more alkaline pH values. The reported maximum sorption capacity of amorphous ferric hydroxide is 8.6×10^{-2} moles arsenate/mole $Fe(OH)_3$ (Beak, 1986). In the present case of initial dissolved iron to arsenate ratios of 1.2, adsorption to ferric hydroxide could account for about 10% removal of arsenate from the solution. Indeed, substantially higher Fe/As ratios than present in the raffinate would be required to bring about significant arsenate sorption to ferric hydroxide.

In a recent review, Robins (1985) has addressed the potential formation of iron(III) - arsenic(V) precipitates other than simple ferric arsenate. It appears that basic arsenates ($FeAsO_4 \times Fe(OH)_3$) reflect a combination of adsorption and precipitation mechanisms rather than being stable solid phases. Thus, dissolved arsenic removal from solutions with iron(III) results in the formation of ferric arsenate ($FeAsO_4$) while ferric hydroxide provides additional removal at pH 2 to pH 6. In solutions containing calcium ions, a precipitate containing approximately 1:1:1 molar ratios of Ca:Fe (III):As(V) has been found, but could not be identified by X-ray diffraction. In any case, the solubility of this precipitate was similar to ferric arsenate and was stable only in the low pH region.

For $FeAsO_4$ precipitation in raffinate solution, the arsenic concentration is estimated as follows. If the pH is below that of the formation of ferric hydroxide ($Fe(OH)_3$) precipitate, the following equations were used:

$$[As_T] = \frac{[As]_{T,0} - [Fe]_{T,0} + \left(([As]_{T,0} - [Fe]_{T,0})^2 + 4\,K\right)^{1/2}}{2}$$

$$K = \frac{(10^{-20.26}+10^{-(8.42+pH)}+10^{-(1.53+2pH)}+10^{1.82-3pH})(1+ f_3 f_2 * 10^{3.02}\,[SO4] \;\ldots\; + \frac{f3}{f2}\,10^{pH-2.19})}{f_3{}^2}$$

where:

$[As]_T$ = arsenic concentration in moles/L

$[As]_{T,0}$ = initial concentration of dissolved arsenic

$[Fe]_{T,0}$ = initial concentration of dissolved ferric ion

f_2, f_3 = activity coefficients of divalent and trivalent ions, respectively.

If the pH is sufficiently high to give amorphous ferric hydroxide as a second precipitate, the dissolved arsenic concentration becomes:

$$[As]_T = \frac{(10^{-20.26} + 10^{-(8.42 + pH)} + 10^{-(1.53 + 2pH)} + 10^{1.82-3pH})}{f_3\; 10^{5.97\;-3pH}}$$

In the above equation, the term $10^{5.97-3pH}$ represents the activity of the ferric ion in equilibrium with the ferric hydroxide precipitate.

There is also a possibility that ferric arsenite ($FeASO_3$) also precipitates by the same mechanisms. The solubility will be greater than for $FeAsO_4$ and as such does not support the analytical results for low arsenic levels in the pH 3-5 range.

7.4.4 Fe(II) - Arsenic(V) Precipitation

The solubility of ferrous arsenates has been briefly reviewed by Robins (1985). The removal of arsenates from solution as iron(II) arsenates has not been studied in detail. Generally, attempts to remove arsenate from solutions involves dosing with ferrous iron followed by aeration to oxidize the iron to the ferric state. However, the solubility of ferrous arsenate

($Fe_3(AsO_4)_2$) is substantially less than the solubility of ferric arsenate. Furthermore, the solid phase $Fe_3(AsO_4)_2$ (s) appears to be stable between pH 4 and pH 10 under non-oxidizing conditions. As stated by Robins (1985), the precipitation of arsenate as ferrous arsenate may be a more efficient means of reducing the arsenate concentration than the conventional precipitation reaction as ferric arsenate.

The Key Lake raffinate solution is believed to contain significant concentrations of ferrous ion. This is reflected by the high concentrations of iron at pH 5 in the limed raffinate experiments. The observed concentration of 910 mg/L total dissolved iron, for example, is several orders of magnitude higher than concentrations expected for dissolved iron (III) only. It is, therefore, worthwhile to examine the solubility of $Fe_3(AsO_4)_2$ in Key Lake raffinate solutions. The relevant solubility product may be defined as follows:

$$Fe_3(AsO_4)_2\ (s) \quad \text{---->} \quad 3\ Fe^{2+} + 2AsO_4{}^{3-}$$

$$(Fe^{2+})^3\ (AsO_4{}^{3-})^2 = Kso \qquad \log Kso = -40.85$$

The activity of the trivalent arsenate in limed Key Lake raffinate solutions can be expressed as shown in Section 7.4.2. The dissolved ferrous ion speciates as the sulphate complex:

$$Fe^{2+} + SO_4{}^{2-} \quad \text{---->} \quad FeSO_4{}^{o}(aq) \qquad \log K = 2.3$$

The concentrations of the hydroxo complexes ($Fe(OH)^{+1}$, $Fe(OH)_2^o$ aq) are insignificant at pH values below pH 9. The mole fraction of the ferrous ion in solution at an ionic strength of 0.2M is given by:

$$\frac{[Fe^{2+}]}{[Fe]_T} = \frac{1}{1 + 10^{1.39}\ [SO_4{}^{2-}]}$$

The activity of the ferrous ion, in terms of total iron in solution can be expressed as:

$$(Fe^{2+}) = \frac{f_2\,[Fe]_T}{1 + 10^{1.39}\,[SO_4^{2-}]}$$

For calculation purposes, we shall assume that total ferrous iron and total arsenic are initially present in their stoichoimetric ratios of 3:2. It follows, therefore, that the total ferrous ion remaining in solution can be expressed as the function of the total arsenate ($[As]_T$) as indicated below:

$$[Fe]_T = \frac{3}{2}\,[As]_T$$

The combination of the above relationship with the solubility product expression gives the following for total dissolved arsenate concentration in equalibrium with $Fe_3AsO_4(s)$:

$$[As]_t = \frac{(2/3)^{3/5}\,Kso^{1/5}\,(1+10^{11.84-pH}+10^{18.73-2pH}+10^{22.08-3pH})^{2/5}(1+10^{1.39} \ldots\ldots [SO_4{}^{2-}])^{3/5}}{f_2{}^{3/5}\,f_3{}^{2/5}}$$

The results are provided in Table 7-6. It is noteworthy that the predicted concentration falls below the observed concentrations above pH 6. Robins (1985) has noted that the formation of mixed Fe(II)/Fe(III) arsenates can occur. These mixed arsenates would have solubilities between the end members, $FeAsO_4$ and $Fe_3(AsO_4)_2$.

It is likely, that either ferrous arsenate or a mixed Fe(II)/Fe(III) arsenate indeed form during liming between pH values above 3.0. However, the initial iron to arsenic ratios in the raffinate solution is not sufficient for forming iron arsenates only. It is most likely that the precipitation products at this pH range include both iron and aluminum arsenates. The relative ratio of iron and aluminum compounds cannot be assessed.

TABLE 7-6

PREDICTED ARSENIC CONCENTRATIONS FOR $Fe_3(AsO_4)_2$ PRECIPITATION

	As (mg/L)	
pH	Model Prediction	Raffinate Concentration
2	> 2100	2100
4	47	-
5	6.9	3.3
6	1.1	3.2
7	0.17	4.5
8	0.03	5.8
9	0.005	3.9
10	0.002	3.1

7.4.5 Calcium - Arsenic(V) Precipitation

Arsenate is known to precipitate as calcium arsenate at alkaline pH values. After oxidative pretreatment to oxidize As(III) to As(V), arsenates can be removed as calcium arsenates by liming process solutions. The precipitation reaction of the calcium-arsenic(V) system has been studied by Nishimura and Tozawa (1985). At pH values below 12, the stable solid phase is $Ca_3(AsO_4)_2 \cdot Ca(OH)_2$, while at pH values above 12, calcium arsenate ($Ca_3(AsO_4)_2$) is more stable. The solubility equilibrium of $Ca_3(AsO_4)_2 \cdot$-$Ca(OH)_2$ can be expressed as follows:

$$Ca_3(AsO_4)_2 \cdot Ca(OH)_2 \text{ ---> } 4Ca^{2+} + 2\ AsO_4^{3-} + 2OH^-$$

The activity of the arsenate (AsO_4^{3-}) ion can be expressed as follows (Nishimura and Tozawa, 1985):

$$[AsO_4^{3-}] = \frac{10^{0.88-pH}}{\{Ca^{2+}\}^2}$$

Expressing activities in terms of total arsenic (and calcium) concentrations, the concentration of total arsenic ($[As]_T$) in solution becomes:

$$[As]_T = \frac{10^{0.88-pH}\ (1 + 10^{11.84-pH} + 10^{18.73-2pH} + 10^{23.08-3pH})}{f_3 f_2^2\ [Ca^{2+}]^2}$$

where:

$[Ca^{2+}]$ = concentration of calcium in solution

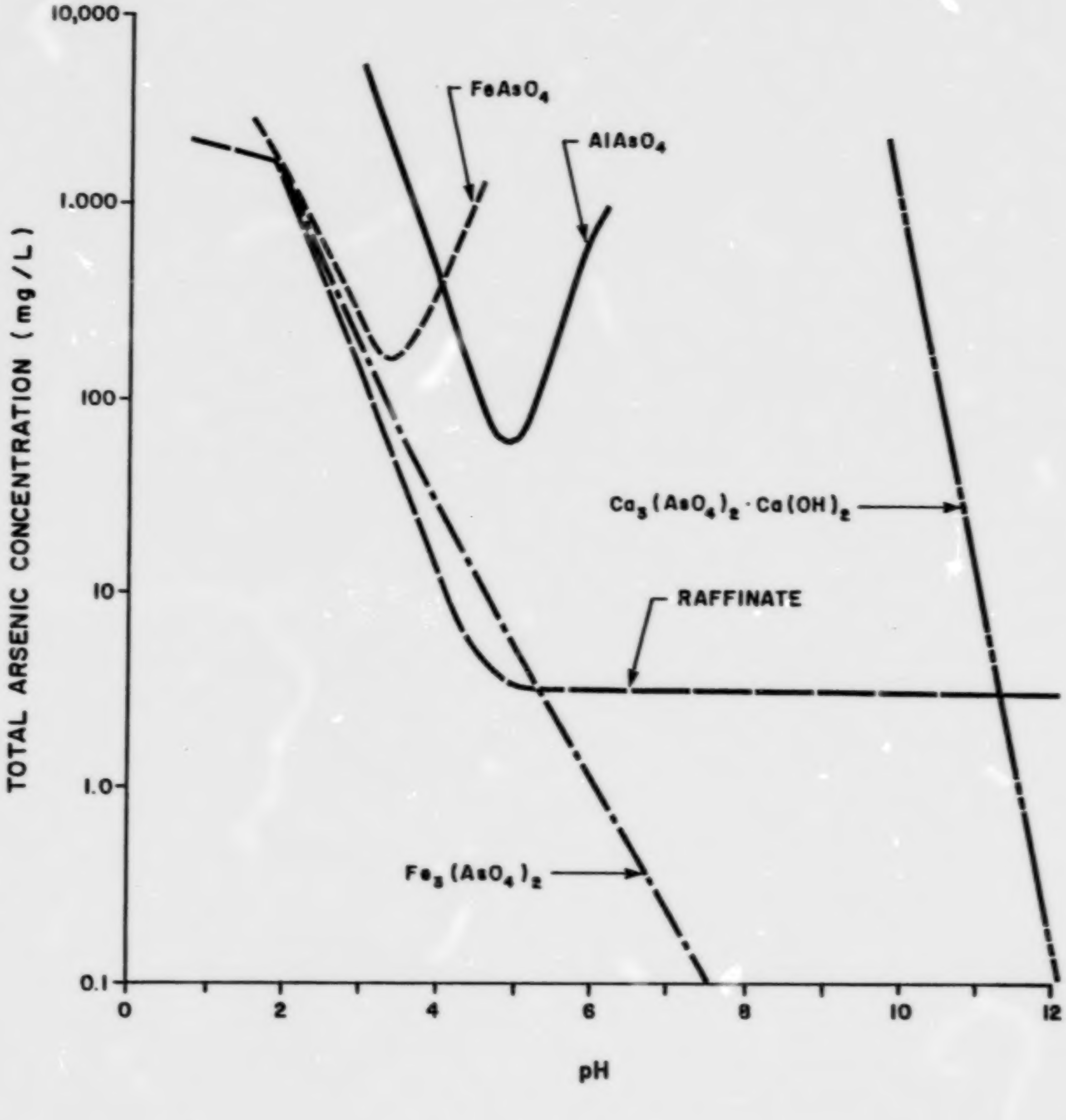
Since calcium is added during liming of the raffinate, the above equation may be used without consideration of the stoichoiometry of precipitation. The results are shown on Figure 7-4 (Section 7.4.6). It is evident, that calcium arsenates are stable at pH values above 10. At high pH values, iron and aluminum arsenates would dissolve and reprecipitate as calcium arsenates. At Key Lake the tailings discharge water is at pH 11 or greater whereas the pH of tailings porewater is in the range of 7 to 10. This would lead to some re-dissolution of calcium arsenate in the tailings with re-precipitation of the arsenate in some other form.

7.4.6. Geochemical Model

The species controlling arsenic precipitation in the Key Lake raffinate and tailings has not been identified. However, a geochemical model which assumes arsenic is controlled by a mixed metal arsenate precipitate is supportable. The arsenic solubility of precipitates along with the levels measured in limed raffinate are illustrated in Figure 7-4. Of prime importance may be the ferrous arsenate precipitate. It appears that although $Fe_3(AsO_4)_2$ is capable of reducing dissolved arsenic to very low levels, the on-going oxidation of iron(II) to iron(III) may maintain arsenic in solution. Alternatively, adsorption on hydroxides may also control the long-term solubility of arsenic in combination with the metal arsenite precipitate.

FIGURE 7.4

GEOCHEMICAL MODEL FOR ARSENIC



7.5 GEOCHEMICAL MODEL FOR NICKEL

7.5.1 General

Nickel chemistry is poorly understood and this is especially true in acidic, high sulphate solutions. Data on nickel precipitation from Key Lake tailing solutions indicates that nickel concentrations reach about 1.0 mg/L at pH levels of 7 and seepage and porewaters in the 7-9 pH range average some 0.1 to 0.5 mg/L. This data is not consistent with the raffinate precipitation results in this study and suggests some other solid phase is controlling nickel concentrations.

Raffinate precipitation with lime indicates that nickel precipitation begins in the pH 5 to pH 6 range. Levels of nickel are typically 1 to 2 orders of magnitude higher than those reported for tailings solutions. The reason for this difference are not clear but would tend to suggest that the amorphous precipitate formed initially becomes more stable (crystalline) with time. This aging effect on the stability of metal hydroxides is well known. Thus, nickel would precipitate initially as the more soluble (amorphous) "alpha" form, but converts to the more stable beta $Ni(OH)_2$ upon aging.

Based upon this study, the Key Lake modelling work (Knight and Piesold, 1985) and the recent Beak (1986) study it was concluded there are two or three plausible models for nickel control. The first involves beta $Ni(OH)_2$ precipitation, the second a nickel hydroxysulphate precipitation, and the third a nickel ferrite precipitation as described by Beak (1986).

7.5.2 Beta $Ni(OH)_2$

The generally accepted stable solid phase for nickel under alkaline condition is nickel hydroxide. Using the equilibrium and stability constant data (corrected for ionic strength) on Table 7-1 the following solubility relationship can be developed:

$$Ni_{(T)} = 10^{(11.2-2pH)} + 10^{(0.9-pH)} + 10^{(-9.2)} + 10^{(pH-20.2)}$$

where:

$(Ni)_T$ = nickel concentration in moles/L.

The model predictions versus pH are compared with raffinate data and Key Lake tailings in Table 7-7. As can be seen, below a pH level of 8 the beta nickel hydroxide model over predicts nickel solubility for both raffinate and tailings by as much as 1 to 3 orders of magnitude. Certainly above pH levels of 8 the nickel hydroxide model appears to be valid.

7.5.3 Nickel Sulphate

SENES originally proposed that nickel solubility may well be controlled by sulphate complexes in tailings water with high sulphate concentrations. It is believed that nickel will precipitate as nickel hydroxysulphate and have a general formula of:

$$m\ Ni(OH)_2 \cdot n\ NiSO_4.$$

The solubility product (Kso) for nickel hydroxysulphate is in the order of 10^{-13} (Smith and Martel, 1976). The general formula for calculating the solubility of a mixed precipitate is:

$$[Ni] \cdot \left[\frac{2\,m}{n+m}\right][OH] \cdot \left[\frac{n}{n+m}\right] \cdot [SO_4]$$

Using the stability relationships for nickel(II) complexes, the following geochemical model for nickel was developed:

$$Ni_T = 10^{(1-XpH)} \times (1 + 10^{(pH-10.15)} + 10^{(2pH-18.25)} + 10^{(3pH-31.35)} \times (SO_4)^{-y}$$

where: $X = \dfrac{2m}{n+m}$ $y = \dfrac{n}{n+m}$

TABLE 7-7

NICKEL HYDROXIDE MODEL PREDICTIONS

	Ni(mg/L)		
pH	Beta $Ni(OH)_2$ Model Results	Limed Raffinate Results	Key Lake Tailings Data
6	>3000	1600	>100
7	88	13	<0.1-0.3
7.5	8.8	-	<0.1*
8.0	0.88	2.6	<0.1
9.0	0.01	0.61	<0.1

* values for seepage, some adsorption in collection system is possible.

For the raffinate solution, a best fit of the data corresponds to X = 0.8 and y = 0.6. The model predictions for $Ni(OH)_2.SO_4$ complex are compared with limed raffinate results and Key Lake tailings data in Table 7-8. As can be seen, the nickel hydroxysulphate model describes raffinate data very well over the pH range 7 to 9 and suggests this may well be the solid phase controlling precipitation. The model does not support the low levels for nickel measured in tailings water. This again may be due to the precipitation of alpha nickel hydroxide in the complex which becomes more stable over time (as would occur in a tailings basin).

7.5.4 Nickel Ferrite Precipitation

Nickel ferrite cannot be ruled out as a potential solubility control in the Key Lake tailings. The raffinate data, however, confirm that nickel does not appear to be precipitated with iron. Beak (1986) have shown nickel ferrite in equilibrium with goethite has solubility similar to beta nickel hydroxide. However, if in equilibrium with amorphous ferric hydroxide, the solubility is lowered by some 7 orders of magnitude.

7.5.5 Proposed Model

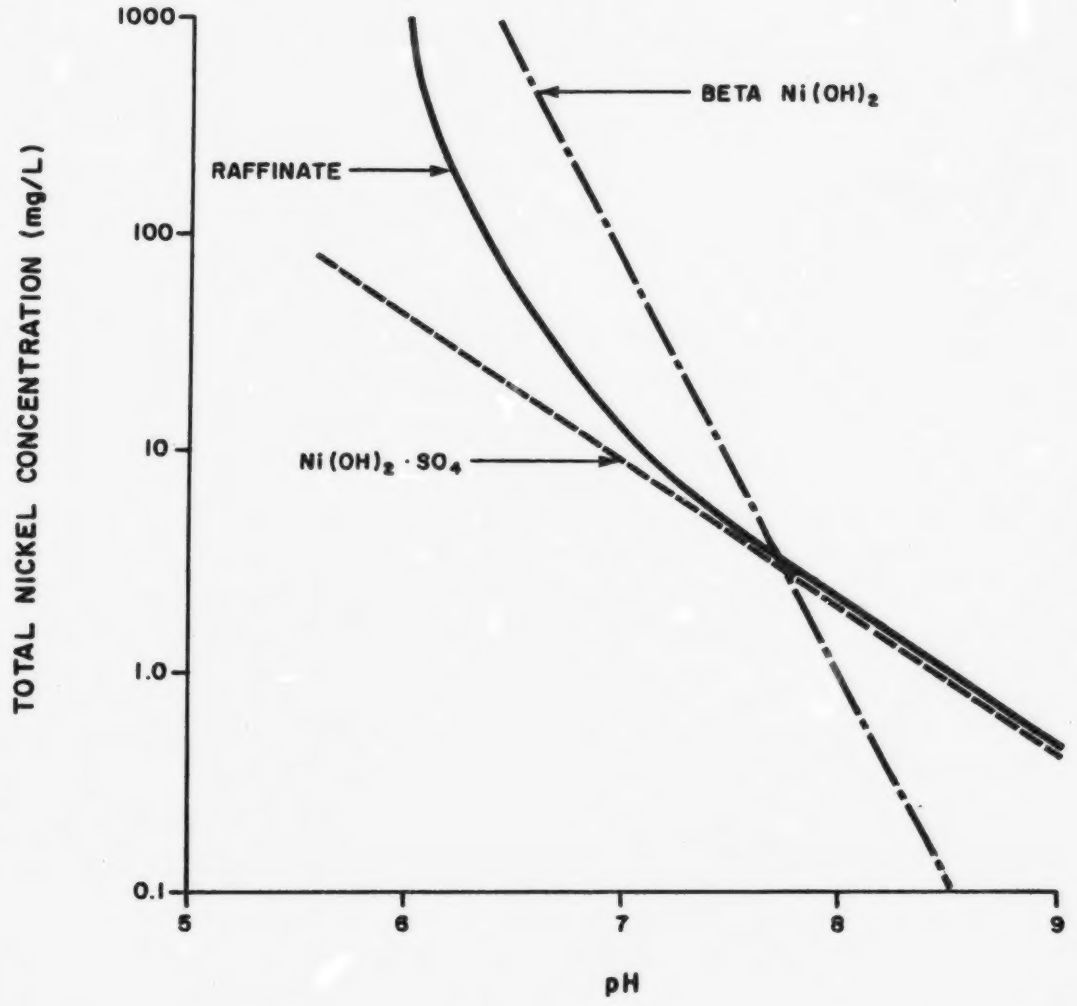
The species controlling nickel solubility has not been identified. However a model which assumes beta nickel hydroxide as the stable species above pH levels of 8 is supportable. Below pH levels of 8 the nickel hydroxide sulphate model describes the data but there is little evidence to support its application. Sulphate levels are a key to the solubility of this complex. The geochemical model for nickel is presented in Figure 7-5.

TABLE 7-8
NICKEL HYDROXIDE-SULPHATE MODEL PREDICTIONS

	Ni(mg/L)		
pH	$Ni(OH)_2-SO_4$ Model Results	Limed Raffinate Results	Key Lake Tailings Data
6	47	1600	>100
7	10	13	<0.1-0.3
8	2.3	2.6	<0.1
9	0.72	0.61	<0.1

FIGURE 7.5

GEOCHEMICAL MODEL FOR NICKEL



8.0 CONCLUSIONS AND RECOMMENDATIONS

A nickel/arsenic metallurgical balance for the Key Lake milling circuit has indicated that approximately 55% of the nickel and 60% of the arsenic in the Key Lake tailings are present in the form of chemical precipitates produced in the waste treatment circuit.

Mineralogical investigations of the precipitates formed however have not proven to be successful in identifying any of the nickel or arsenic solids that may control their long-term dissolution. No crystalline nickel or arsenic precipitates could be determined by X-ray diffraction, which would indicate that the precipitates are amorphous substances. Qualitative elemental analysis using transmission electron microscope attached to an EDAX system and an electron microprobe attached to an ADAX system has indicated that the yellow-brown, amorphous material consists of iron, nickel, arsenic and lesser amounts of aluminum and silica. Analysis of a series of precipitates by Raman microprobe analysis gave a weak Raman band corresponding to iron(III) arsenates. Although a number of other bands were observed, aside from those of gypsum, they could not be identified with any other mineral.

The geochemical models for arsenate precipitation reactions from the limed raffinate solutions suggest that iron(III) arsenates, aluminum arsenates, and iron(II) arsenates form sequentially as the pH is adjusted from the initial pH value of pH 2. Iron(III) and aluminum arsenates are thermodynamically unstable at pH values above 6 in as much as these metal arsenates would decompose to their respective hydroxides. However, the occlusion of these arsenates in precipitated gypsum or metal hydroxides may give rise to metastable conditions. In this case, solubility would depend on the dissolution of the host (i.e. enveloping) mineral.

Iron(II) arsenates appear to be stable in the pH range of 6 to 10 in anoxic conditions. However, the iron to arsenic ratio in the raffinate is insufficient to precipitate all the arsenate as $Fe_3(AsO_4)_2$. An interesting possibility is the formation of mixed Fe(II)/Fe(III) arsenates with solubilities between $FeAsO_4$ and $Fe_3(AsO_4)_2$. Calcium arsenates are stable under alkaline conditions above pH 10. At high pH values, iron and aluminum arsenates may dissolve incongruently and arsenate may reprecipitate as $Ca_3(AsO_4)_2 \cdot Ca(OH)_2$.

It seems that the solubility of arsenate is not fully equilibrium controlled. Usually, dissolved arsenate concentrations were at a minimum with short reaction times (0.5 hours) after pH adjustment and showed an increasing trend with time. However, the final values remained orders of magnitude below the "equilibrium" values with respect to Fe(III) or Al(III) arsenates.

Although the presence of the arsenite species in the raffinate has been identified chemical model predictions for arsenic have been based on the arsenate ion since this species allows a reasonable interpretation of the test data from a chemical equilibrium point-of-view. Attempts at chemical modelling based on the arsenite species was not possible based on the test data obtained in the testwork. It is quite feasible that during lime neutralization of Key Lake waste solutions iron(III) oxidizes the arsenic(III) species in the raffinate to arsenic(V) leading to reduction of part of the iron in solution to iron(II). Also, based on Eh-pH diagrams, arsenate is the major species present in solution at elevated pH and high redox values. Consequently chemical equilibrium modelling based on the arsenate species is plausible.

The long-term implications of the results of this study for predicting tailings porewater arsenic quality remains somewhat conjectual. It is significant, however, that arsenic concentrations obtained in this experimental program were usually higher than those observed in tailings porewater under similar conditions of pH. This would imply that aging does not have a detrimental effect with regard to the dissolution of arsenate precipitates.

In the anoxic environment of tailings porewater, iron(II) arsenates are thermodynamically stable. On the other hand, the dissolution rates of iron(III) and aluminum arsenates are probably sufficiently low to allow the readsorption of the dissolved arsenate on metal hydroxide surfaces. In addition, dissolved iron(III) may be reduced to iron(II) to allow the reprecipitation of approximately 67% of the iron(III) arsenate as iron(II) arsenate. The combined effect of these mechanisms would yield arsenate concentrations in the mg/L range.

A geochemical model which describes the measured data for nickel has been developed. The model assumes that nickel hydroxide is the predominant species under alkaline conditions and that a nickel hydroxysulphate complex controls solubility below this level. There is strong evidence that nickel precipitates become more stable as they are aged.

Long-term nickel levels in uranium tailings porewater will be a function of seepage pH and sulphate levels. With the elevated gypsum content of the tailings sulphate levels are expected to be elevated for thousands of years. Therefore nickel concentrations in seepage would be expected to fall into the 0.5 to 5 mg/L range for the stable nickel hydroxysulphate complex in a pH range of 6-7.

From the results of this study it is apparent that more detailed laboratory investigations are required to better understand the solution chemistry and to chemically identify the exact nature of the nickel and arsenic precipitates formed in the Key Lake waste treatment circuit. It may well be that this work would need to incorporate aging tests in the hope of achieving some form of crystallinity for the precipitates which would facilitate the identification of the precipitate solids. Unless the nature of the precipitates in the Key Lake tailings can be identified with a reasonable degree of confidence other avenues of investigations would not be warranted.

Additional work is required to verify iron and arsenic speciation in the Key Lake milling circuit. This would include an evaluation of various process streams in the milling circuit as well as waste solutions, tailings porewater and tailings seepage solutions.

Monitoring of Key Lake tailings porewater and seepage should be continued to verify and improve upon the tentative geochemical models that have been put forward for arsenic and nickel.

9.0 REFERENCES

Beak Consultants Limited, 1986. "Geochemical Behaviour of Various Non-Radionuclide Contaminants in Uranium Mill Tailings", Report for the National Uranium Tailings Program.

Chuklantsev, V.G., 1956. "The Solubility Products of Metal Arsenates", Zhur. Anal. Khim., Volume II, pp. 529-535.

Clark, P.J., et al., 1980. "The Key Lake Uranium Process," Nineteenth Annual Conference of Metallurgists, CIM, Halifax, Nova Scotia, August, 1980.

Knight and Piesold Limited, 1985. "Monitoring of the Key Lake Layered Uranium Tailings, Phase I", Report for the National Uranium Tailings Program.

Knight and Piesold Limited, 1986. "Monitoring of the Key Lake Layered Uranium Tailings, Phase II", Report for the National Uranium Tailings Program.

Krause, E. and Ettel, V.A., 1985. "Ferric Arsenate Compounds: Are they Environmentally Safe? Solubilities of Basic Ferric Arsenates", Fifteenth Annual CIM Hydrometallurgical Meeting, Vancouver, Canada, August, 1985.

Neven, M., Steane, R. and Becker, J., 1985. "Arsenic Management and Control at Key Lake", Fifteenth Annual CIM Hydrometallurgical Meeting, Vancouver, Canada, August, 1985.

Nishimura, T. and Tozawa, K., 1985. "Removal of Arsenic From Water by the Addition of Calcium Hydroxide", Fifteenth Annual CIM Hydrometallurgical Meeting, Vancouver, Canada, August, 1985.

Robins, R.G., 1985. "The Aqueous Chemistry of Arsenic in Relation to Hydrometallurgical Processes", Fifteenth Annual CIM Hydrometallurgical Meeting, Vancouver, Canada, August, 1985.

Sherritt Gordon Mines Ltd., 1979. "Extensive Bench Scale Testwork - Appendix D - Volume V", Report to Key Lake Mining Corporation.

Smith, R.M. and Martell, A.E., 1976. "Critical Stability Constants, Volume IV - Inorganic Complexes", Plenum Press, New York, N.Y., U.S.A.

Stumm, W. and Morgan, J.J., 1981. "Aquatic Chemistry", John Wiley and Sons, New York, U.S.A.

APPENDIX A

ORIGINAL STATEMENT OF WORK

Supply and Services Canada Approvisionnements et Services Canada

PAGE 1 OF/DE 2

CONTRACT SERIAL NUMBER / NUMÉRO DE SÉRIE DU CONTRAT

CONTINUATION

DSS FILE NUMBER – NUMÉRO DU DOSSIER MAS: 15SQ.23317-6-1727

APPENDIX "A"

STATEMENT OF WORK

Study of the State of Nickel and Arsenic in Uranium Mill Tailings

OBJECTIVES:

To identify the physical state of nickel and arsenic after uranium ore leaching to help understand the geochemical mechanisms controlling their dissolution in uranium mill tailings

BACKGROUND:

The National Uranium Tailings Program is striving to develop mathematical models to predict future events pertaining to uranium tailings and to quantify and assign uncertainties to these predictions. To do so, data and information on the pathways of release of contaminants from the tailings in the long term are being obtained. Nickel and arsenic are important contaminants in some Saskatchewan uranium ores and a knowledge of their physical state and subsequent dissolution behaviour is necessary to model these elements in uranium mill tailings. At present, there is no evidence for a solid compound that can limit the aqueous concentrations to those observed in nickel and arsenic-bearing tailings systems in the pH range of 6-11 and it is postulated that their adsorption by iron and aluminum hydrous oxides may be the important controlling reaction.

SCOPE OF WORK

The work will include an experimental investigation of the physical state and dissolution behaviour of nickel and arsenic in uranium mill tailings from Key Lake Mining Corp., located in Key Lake, Saskatchewan.

The contractor is resposible for obtaining the uranium mill tailings from Key Lake, Saskatchewan.

The contractor shall undertake the following tasks:

(1) Mass Balance for Nickel and Arsenic

- To attempt a mass balance for nickel and arsenic within the Key Lake uranium circuit. This is not intended to be an exhaustive study but rather one that will provide sufficient information on the physical state and dissolution behaviour of nickel and arsenic.

- To indicate which other elements will be determined because of their relation to the physical state and dissolution behaviour aspects. Iron, calcium, magnesium and aluminum are suggested.

(2) State of Nickel and Arsenic In Precipitate after Neutralization of Solvent Extraction Raffinate

- To collect a sufficient quantity of solvent extraction raffinate before bulk neutralization to perform a series of neutralization or "pH adjustment" tests. Solids, if formed, and leachate will be analyzed for nickel, arsenic and indicated elements.

- To identify the solid phases formed, if in sufficient amount, for example, by X-ray diffraction.

Supply and Services Canada
Approvisionnements et Services Canada

PAGE 2 OF DE 2

CONTINUATION

CONTRACT SERIAL NUMBER NUMÉRO DE SÉRIE DU CONTRAT	DSS FILE NUMBER – NUMÉRO DU DOSSIER DAS
	15SQ.233175-1727

(3) Interpretation of Test Results

- To interpret the test results in terms of possible precipitation-dissolution mechanisms for nickel and arsenic in uranium mill tailings. The application of chemical equilibrium modelling is recommended here.
- To identify shortcomings(i.e., incompleteness, unsuitability, ambiguity, etc.) in the test results and their implication for the proposed precipitation-dissolution mechanisms.

(4) Quality Assurance

- To describe a procedure for quality assurance of the analytical component of this study. The use of duplicate, "blind" and blank samples should be included.

DELIVERABLE ITEMS

Monthly progress reports in letter format are to be submitted in two copies to the Scientific Authority. These reports must summarize:

- work done in the previous period
- significant achievements
- potential problem areas
- the work planned for the next period

Regular reference should be made to the Statement of Work, the project schedule and the cost estimate in the proposal.

A draft final report is to be submitted in three copies to the Scientific Authority on or before August 1, 1986. The Scientific Authority will return one copy with his comments and suggestions to the contractor within two weeks after receiving the draft final report.

The Contractor will present and discuss the results of this work at an information seminar for the National Uranium Tailings Program staff. This seminar will be held in Ottawa on or before August 15, 1986. the date of the seminar will be negotiated between the parties involved at a later date.

Twenty-five copies of the final report are to be submitted to the Scientific Authority on or before August 31, 1986. The final report must also contain an executive summary.

APPENDIX B

MINERALOGY REPORT

APPENDIX B

MINERALOGY OF THIRTEEN PRECIPITATES PRODUCED BY NEUTRALIZATION OF KEY LAKE RAFFINATE

SUMMARY

Thirteen precipitates were examined visually and by a scanning electron microscope. The first twelve precipitates were found to consist of abundant gypsum, some pisoliths (round nodules) of various sizes and colors, and yellow-brown material composed of aggregates of sub-micron size tabular crystals. The shells of pisoliths were composed of a mosaic of crystals with the same morphology and grain size as the yellow-brown material and are probably the same substance.

X-ray diffraction studies showed that the yellow-brown material and the shells of pisoliths are amorphous.

Qualitative element analyses using a transmission electron microscope attached to an EDAX system and an electron microprobe attached to an ADAX system indicated that the amorphous material contained substantial Fe, Ni, As and lesser quantities of Al, Si, and possibly Ca. The fine grain size and poor polishing characteristics of the amorphous material prevented quantitative analyses by the electron probe.

To obtain better information on the chemical constitution of the amorphous material, it was concentrated from four precipitates by dissolving/leaching away gypsum in water. Chemical analyses, expressed as standard oxides, showed that the amorphous residues are hydrous, and can contain up to 37.7% NiO, 25.2% As_2O_3, and 24.5% Fe_2O_3 and lesser quantities of Al_2O_3, SiO_2 and possibly CaO. V, Zn, Co, Cu and Y are present in minor concentrations. An analysis of the leach water from one precipitate indicates that the amorphous material has a relatively low solubility in water, that it dissolves incongruently, and that As is the most soluble metal and is considerably more soluble than Ni (As/Ni=168). The relative solubilities of As and Ni parallel solubilities found previously for Key Lake tailings.

Raman microprobe analysis of a series of precipitates indicates that the yellow-brown amorphous material gives rise to a weak Raman band at the same wave number as the Fe arsenate reference material synthesized in this study.

VISUAL EXAMINATION

The thirteen precipitates submitted for mineralogical examination are listed in Table 1.

Under the optical microscope Precipitates No. 1 to No. 12 were light brown in color and were composed of the same constituent minerals: white needles, laths and plates of gypsum, very fine grained yellow-brown material (later found to be amorphous) scattered throughout the gypsum, pisoliths or spherical nodules measuring from about 0.1 mm to about 10 um in diameter. Crushing the larger pisoliths with a needle showed that they are composed of a white crystalline core (gypsum) and a thin shell made up of a fine grained tabular crystals. The surface of the shells range in color from black to brown to yellow, or combinations of these colors.

Precipitate No. 13 was quite different from the other twelve. It consisted of irregular shaped greenish lumps which were subsequently identified to be magnesium hydroxide or brucite.

SCANNING ELECTRON MICROSCOPE (SEM) EXAMINATION

All thirteen precipitates were examined by the SEM and a series of photomicrographs were taken of each one. The photomicrographs are presented in Figures 1, 2 and 3.

Precipitates No. 1 to No. 12 were made up of the following basic constituents:

- needles, laths and plates of gypsum
- pisoliths of various sizes
- sub-micron tabular grains occurring mainly as aggregates adhering to other mineral grains.

TABLE 1

LIST OF PRECIPITATES FOR MINERALOGICAL EXAMINATION

Precipitate No.	Precipitate Description
1	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 5 for 1 hour.
2	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 6 for 1 hour.
3	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 7 for 1 hour.
4	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 8 for 1 hour.
5	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9 for 1 hour.
6	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 11 for 1 hour.
7	Filter cake from filtrate obtained from treatment of No. 1 above taken to pH 7.
8	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9; with a 2-hour retention time.
9	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9; with a 6-hour retention time.
10	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9; with a 0.5-hour retention time.
11	Filter cake from pre-neutralized (pH 2) raffinate limed to pH 9; with a 24-hour retention time.
12	Stage 1 (pH 7) filter cake from the Key Lake waste treatment circuit simulation test.
13	Stage 2 (pH 11) filter cake from the Key Lake waste treatment circuit simulation test.

Figure 1E shows the various constituent minerals quite clearly. The smooth surfaced gypsum needles, laths and plates have attached aggregates of fine grained tabular crystals. The shell of the pisolith is made up of sub-micron tabular crystals very similar in morphology and crystal size to the tabular crystals comprising the scattered aggregates.

Figure 3C shows that the pisoliths are composed of a core of gypsum crystals covered by a thin shell.

X-RAY DIFFRACTION (XRD) IDENTIFICATION

Smear slide mounts were made from the thirteen precipitates as received. The resulting XRD charts for Precipitates No. 1 to No. 12, were practically identical and indicated the presence of only gypsum (see Figure 4 as an example).

As visual and SEM examination showed that other minerals were present in the precipitates it was concluded that, (1) gypsum had diluted the sample to the extent that other minerals occurred in concentrations below the limit of detectability (a few percent of the material), or (2) that the other minerals were amorphous. Precipitate No. 13 was different from the other twelve (Figure 5) and showed gypsum peaks and two weak broad peaks of brucite suggesting that brucite had poor crystallinity.

A number of pisoliths were removed from the precipitates and were mounted on the ends of glass fibres for powder camera x-ray diffraction. The resulting powder diffraction films showed only the diffraction lines of gypsum. It is concluded that the x-ray patterns were derived from the pisolith cores which were shown by SEM and visual examination to be gypsum. Evidently the shell material, which is obviously different from the core material, did not produce any XRD lines.

TRANSMISSION ELECTRON MICROSCOPE (TEM) EXAMINATION

The TEM facility at the University of Saskatchewan is equipped with an EDAX system that can provide information about the composition of solid materials. The method of mounting the materials on a formvar-coated copper grid dictates that only particles in the low micron size range can be mounted and examined. Consequently the two samples examined (Precipitates No. 1 and No. 4) were dispersed in water and allowed to settle, and a small drop of slurry of each sample containing only the fine grained fraction was placed on a copper grid.

Figure 3D is a photomicrograph of Precipitate No. 4 showing several aggregates of sub-micron size grains. Figure 6 summarizes the EDAX results for the two samples. The results show that the aggregates contain Al, Si, S, Ca, Fe, Ni and As. Although the results are in terms of raw counts, it is apparent that both aggregates analysed contain appreciable concentrations of all these elements; however, it is apparent that Precipitate No. 4 contains high Ni relative to As and that Precipitate No. 1 shows the reverse relationship. A high As/Ni ratio in Precipitate No. 4 and a low ratio in Precipitate No. 1 is consistent with the As and Ni concentrations in the original precipitates.

It is possible that at least some of the Ca and S may be explained by admixed gypsum. The results indicate that the concentrations of Si, Al and Fe are variable from one sample to the other.

CONCENTRATION OF INSOLUBLES FROM PRECIPITATES NO. 1, NO. 4, NO. 5 AND NO. 7

The TEM work indicated that material containing Ni and As could be separated from gypsum by suspension/leaching in water. Consequently four precipitates (No. 1, No. 4, No. 5 and No. 7) were dispersed in water to dissolve and remove gypsum. A yellowish-brown residue remained.

The residues (No. 1W, No. 4W, No. 5W and No. 7W) were examined by XRD to determine if gypsum had been removed. A very small bassanite peak was found in two residues, probably due to the fact that some dissolved calcium sulphate in the wet residue recrystallized to bassanite when the residue was oven dried (No. 5W, No. 7W, see Figure 7).

The XRD charts (Figure 7) of the four residues showed diffraction patterns without any distinct diffraction peaks (other than weak bassanite peaks) indicating (1) that gypsum had been largely removed and (2) that the yellow-brown residue that remained is amorphous.

The four residues were also examined by the SEM. The photomicrographs of residues No. 5W and No. 4W are shown in Figures 3E and 3F, respectively. The residues are made up of sub-micron size crystals whose morphology and crystal size are very similar to the aggregates of fine grained crystals observed in Precipitates No. 1 to No. 12, and the shells of pisoliths (see Figure 1E for example).

Based on the similarities of crystal morphology and grain size, it is tentatively concluded that the yellow-brown residues, the aggregates of crystals scattered throughout the precipitates, and the materials comprising the shells of pisoliths are the same substance.

ELECTRON MICROPROBE ANALYSIS OF THE INSOLUBLE RESIDUES

An electron microprobe investigation was performed on six precipitates and four residues. Figure 8A shows typical results when the electron beam was focussed on the surface of pisoliths or on selected areas in clumps of gypsum crystals. The EDAX charts show that the areas irradiated contain relatively high concentrations of Ca, Fe, Ni, As with lesser concentrations of Si, Al, S, and sometimes V; basically the same results as were obtained from the analysis of aggregates of fine grained crystals by the EDAX system attached to the TEM. The strong count responses for Ca and S are due to gypsum.

An electron microprobe investigation was attempted of the four residues (No. 1W, No. 4W, No. 5W, No. 7W) that contained little or no gypsum/bassanite. The results (Figure 8B, for example) indicated that these materials contained a moderate amount of Al, Si, Ca, a little V, and a relatively high concentration of one or more of Fe, As and Ni. The concentrations of As and Ni varied from sample to sample.

Unfortunately, it was not possible to do quantitative analyses with the electron microprobe as the minerals were soft and could not be adequately polished in the plastic mounts. No polished reflective surfaces could be produced (except for gypsum) so the analytical results are derived from rough irregular grain surfaces which could not be identified visually. The second problem was that the effective diameter of the electron excited volume under the electron beam exceeded the diameter of the grains by a wide margin (with the exception of large pisoliths) with the result that the line intensities could not be quantitatively related to the line intensities of standards.

For this reason an effort was made to obtain analytical information from the residues by wet chemical analysis.

ANALYSIS OF INSOLUBLE RESIDUES AND LEACH WATER FROM PRECIPITATE NO. 5W

The analysis of the insoluble residues after removal of gypsum by leaching, and of one sample of leach water (No. 5) are summarized in Table 2. The

TABLE 2

ANALYSIS OF RESIDUES AND LEACH WATER

Preparation: Precipitates No. 1, No. 4, No. 7 were repeatedly leached by cycles of washing/centrifuging (up to 15 times). A one gram sample of precipitate No. 5 was stirred continuously for 72 hours in 1 litre of de-ionized water. All residues were dried at 50 to 60°C. Only one sample (No. 5) of leach water was analysed.

	Residue (%)				Leach Water (mg/L)
	No. 1W	No. 4W	No. 5W	No. 7W	No. 5W
Al	8.7	4.9	3.4	0.1	0.4
Si	3.5	1.9	2.2	0.7	0.8
S	-	-	0.41	-	-
Ca	0.1	1.8	2.6	0.1	134.0
Fe	12.1	12.4	7.5	17.1	0.07
Ni	2.2	17.6	11.4	29.6	0.02
As	19.1	9.7	7.1	0.4	3.36
V	0.4	0.2	0.1	0.01	-
Zn	0.2	0.4	0.3	0.6	-
Co	0.04	0.2	0.2	0.5	-
Cu	0.4	0.3	0.2	0.05	-
Y	0.3	0.2	0.2	0.1	-
LOI*	30.0	30.0	42.0	35.0	-

* Loss on ignition at 900°C. Analysis of residue No. 5W for As after firing indicated that As was not vaporized.

Analyses Expressed as Oxides

	Oxide (%)			
	No. 1W	No. 4W	No. 5W	No. 7W
Al_2O_3	16.4	9.3	6.4	0.2
SiO_2	7.5	4.1	4.7	1.5
SO_4	-	-	1.2	-
CaO	0.1	2.5	3.6	0.1
Fe_2O_3	17.3	17.7	10.8	24.5
NiO	2.7	22.4	14.5	37.7
As_2O_3	25.2	12.8	9.4	0.5
V_2O_5	0.7	0.4	0.2	0.02
ZnO	0.3	0.5	0.4	0.8
Co_3O_4	0.1	0.3	0.3	0.7
CuO	0.5	0.3	0.3	0.1
Y_2O_3	0.3	0.3	0.2	0.2
LOI	30.0	30.0	42.0	35.0
TOTAL %	101.1	100.7	94.0	101.3

residues were dissolved in acid and analysed by atomic absorption spectroscopy. Wavelength scans of the solutions indicated a number of additional elements occurring in significant concentrations (Zn, Co, Cu, Y). All these elements have been previously reported for Key Lake ores.

The analytical results show that the insoluble residues contain relatively high concentrations of one or more of Fe, Ni and As. The small concentration of S in No. 5W may be due to residual gypsum/bassanite (see XRD chart Figure 7). The generally low Ca concentrations suggest that Ca is only a minor component of the residue.

The low sulfur concentration (No. 5W) suggests that the compound is not a sulfate. The relatively large loss on ignition (LOI) values probably indicate that the residue is hydrous. If the metals are expressed as standard oxides (Table 2), the analyses of the residues total between 94.1 and 101.5% which are reasonable results. The results suggest then that the residues may be a mixture of metal oxides and hydroxides.

The water from leaching Precipitate No. 5 contains abundant calcium, most of which can be attributed to dissolved gypsum. The concentration of As is considerably greater than Ni giving an As/Ni ratio of 168. It is interesting to note that this value is similar to the ratio of 175 obtained from leaching Key Lake tailings in water (Arnold, 1986[*]). This agreement may be a coincidence, as the ratio obtained would no doubt be influenced by the As/Ni ratio in the residue, which is different from one residue to another.

---

[*] Mineralogy of Key Lake Tailings samples B1 and B3. Prepared for Knight & Piesold Ltd., January, 1986.

EXAMINATION OF THE PRECIPITATES BY RAMAN SPECTROSCOPY

Six reference compounds, listed in Table 3, were prepared according to the procedure given in Appendix B. These were used in attempting to identify the make-up of the precipitates by Raman Spectroscopy.

The Raman microprobe analysis was done by the Mineral Exploration Research Institute using the Raman microprobe in the Department of Chemistry, McGill University, Montreal, Quebec. The XRD charts for these standards are shown in Figures 9 and 10. All the reference materials, with the exception of R-4, were essentially amorphous. Only R-4 showed a reasonable crystallinity, but the pattern could not be identified in the available XRD mineral files.

Because of the mineralogical similarity of Precipitates No. 1 to No. 12, and the time required to undertake Raman microprobe investigation, only Precipitates No. 1, No. 4, No. 5 and No. 7, along with the six reference standards, were examined. The Raman spectra are shown in Figures 11 and 12. The Raman spectra for the six reference materials are shown in Figure 13.

The results of the investigation show that the needles, laths and plates occurring in all precipitates are gypsum.

The yellow-brown material adhering to gypsum crystals in all precipitates gave rise to a weak Raman band at about 324-326 cm^{-1} which was interpreted as an Fe arsenate based on the spectrum of the Fe arsenate reference material R-1. R-1 reference material gave rise to only one medium intensity Raman band (Figure 13).

It is not clear whether the yellow-brown material is all or only partly Fe arsenate. Both the yellow-brown material and reference material R-1 behaved in a similar way when irradiated by the focussed laser beam; they both melted. This problem was remedied by defocussing the laser beam.

Irradiating the surface of pisoliths produced the Raman bands of gypsum, and a weak Raman band of Fe arsenate (at 324-326 cm^{-1}).

TABLE 3

REFERENCE STANDARDS FOR RAMAN MICROPROBE ANALYSIS

Standard No.	Chemical Compound
R-1	Ferric Arsenate (pH 5)
R-2	Calcium Arsenate (pH 9)
R-3	Nickel Arsenate (pH 9)
R-4	Magnesium Arsenate (pH 9)
R-5	Nickel Hydroxide (pH 9)
R-6	Calcium Arsenate (pH 11)

There is a suggestion that small quantities of anhydride ($CaSO_4$) and anorthite (feldspar; $CaAl_2Si_2O_8$) may occur in some of the precipitates. But these are only tentative identifications. There were also a number of Raman bands that could not be identified.

FIGURE 1 CAPTIONS

Figure 1A Precipitate No. 1 showing a pisolith about 45 um in diameter, a clump of gypsum needles, laths and plates with aggregates of fine grained crystals adhering to gypsum (1050 X).

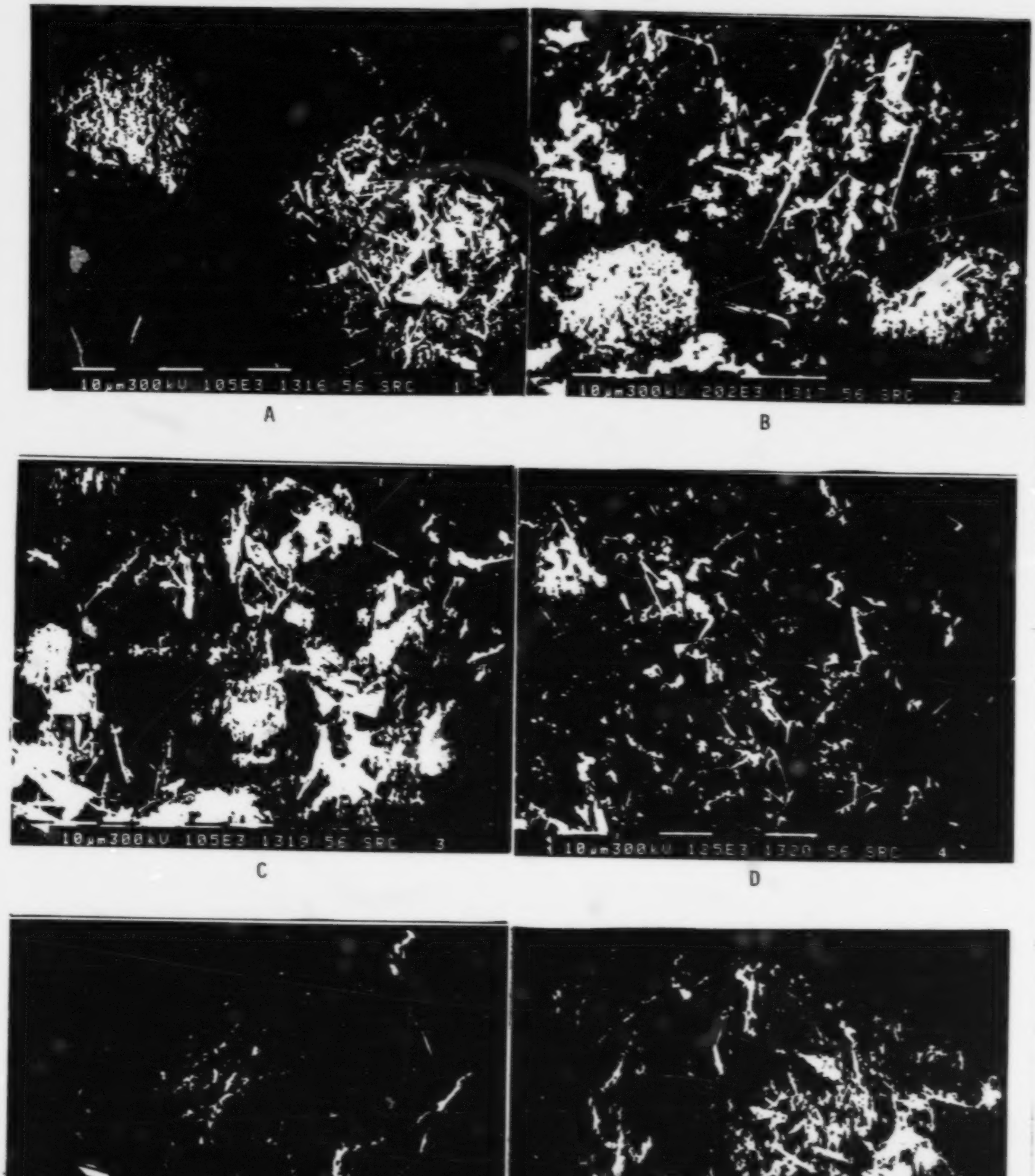
Figure 1B Precipitate No. 2 showing a pisolith about 18 um in diameter, needles, laths and plates of gypsum, and aggregates of fine grained crystals attached to gypsum crystals (2020 X).

Figure 1C Precipitate No. 3. Description is as for Figure 1B but there is no pisolith in the field of view (1050 X).

Figure 1D Precipitate No. 4. The description is the same as for Figure 1B. The pisolith is about 15 um in diameter (1250 X).

Figure 1E Enlargement of pisolith in Figure 1D showing very clearly the gypsum needles, laths and plates with attached aggregates of fine grained tabular crystals. The morphology and crystal size of the fine grained aggregates are very similar to the crystal mosaic comprising the shell of the pisolith (4020 X).

Figure 1F Precipitate No. 5. Description is similar to that for Figure 1B but there is a higher concentration of the aggregates of fine grained crystals attached to gypsum crystals. At top centre is a gypsum rosette which may have been the core of a pisolith (885 X).


10µm300kV 105E3 1316 56 SRC 1
10µm300kV 202E3 1317 56 SRC 2
10µm300kV 105E3 1319 56 SRC 3
10µm300kV 125E3 1320 56 SRC 4
10µm300kV 402E3 1321 56 SRC 4
01mm300kV 005E1 1317 56 SRC 5

A

B

C

D

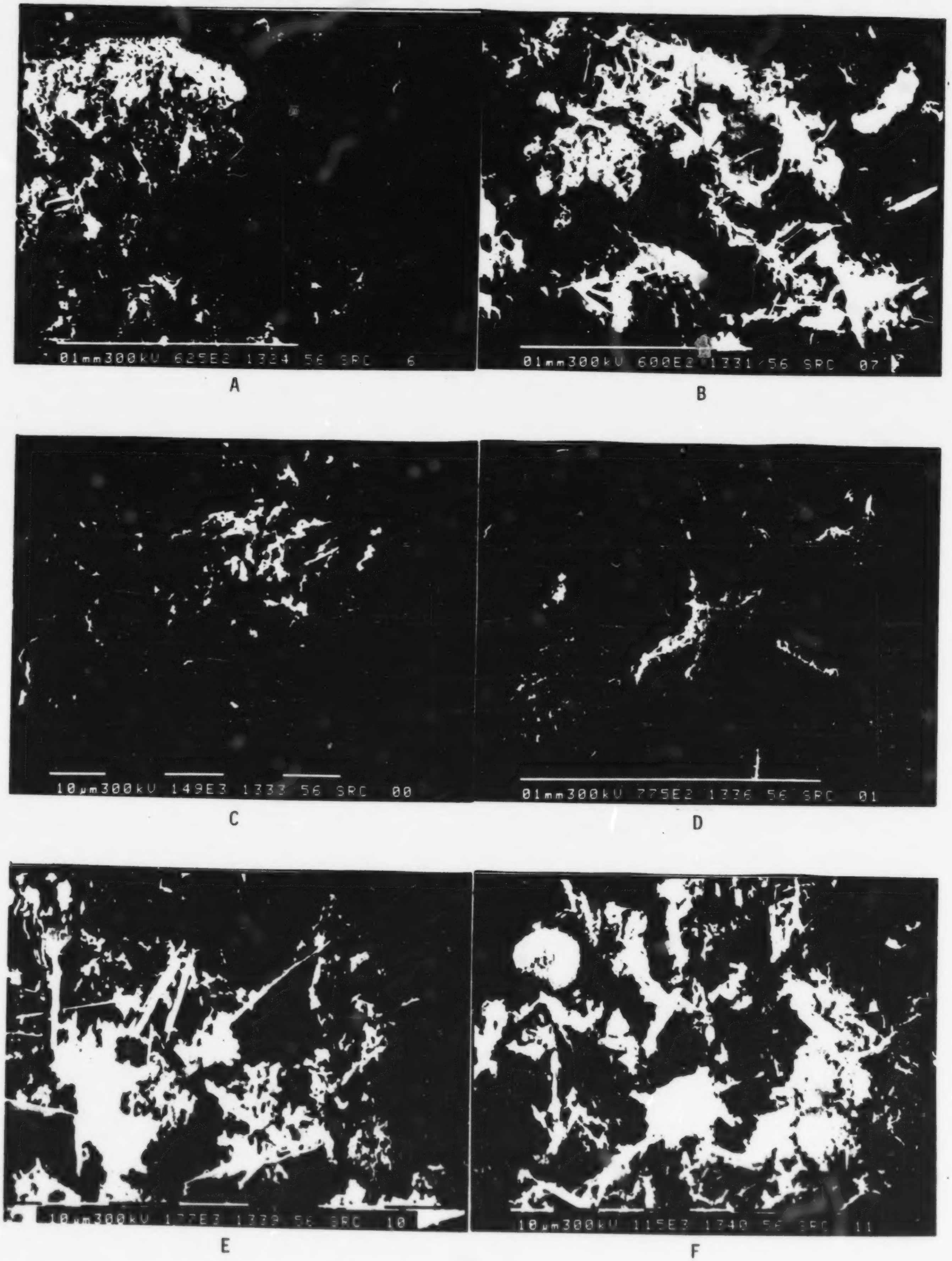
E

F

FIGURES 1A TO 1F

FIGURE 2 CAPTIONS

Figure 2A	Precipitate No. 6. Photo shows a large pisolith about 0.1 mm in diameter and needles, laths and plates of gypsum coated with aggregates of fine grained crystals which are not well resolved at this low magnification (625 X).
Figure 2B	Precipitate No. 7. Gypsum needles, laths and plates and aggregates of fine grained crystals coating some gypsum crystals (600 X).
Figure 2C	Precipitate No. 8. Description is the same as for Figure 2B (1490 X).
Figure 2D	Precipitate No. 9. Description for the right half of the photo is the same as for Figure 2B. The left half of the photo shows masses of the fine grained crystal aggregates which may have been the shell of a ruptured pisolith (775 X).
Figure 2E	Precipitate No. 10. Description is the same as for Figure 2B. The pisolith is about 10 um in diameter (1770 X).
Figure 2F	Precipitate No. 11. Description is the same as for Figure 2B. The pisolith is about 15 um in diameter (1150 X).


01mm300kV 625E2 1324 56 SRC 6
01mm300kV 600E2 1331/56 SRC 07
10µm300kV 149E3 1333 56 SRC 00
01mm300kV 775E2 1336 56 SRC 01
10µm300kV 177E3 1339 56 SRC 10
10µm300kV 115E3 1340 56 SRC 11

A B

C D

E F

FIGURES 2A TO 2F

FIGURE 3 CAPTIONS

Figure 3A Precipitate No. 12. Photo shows the needles, laths and plates of gypsum, several pisoliths just over 10 um in diameter and aggregates of fine grained crystals (1360 X).

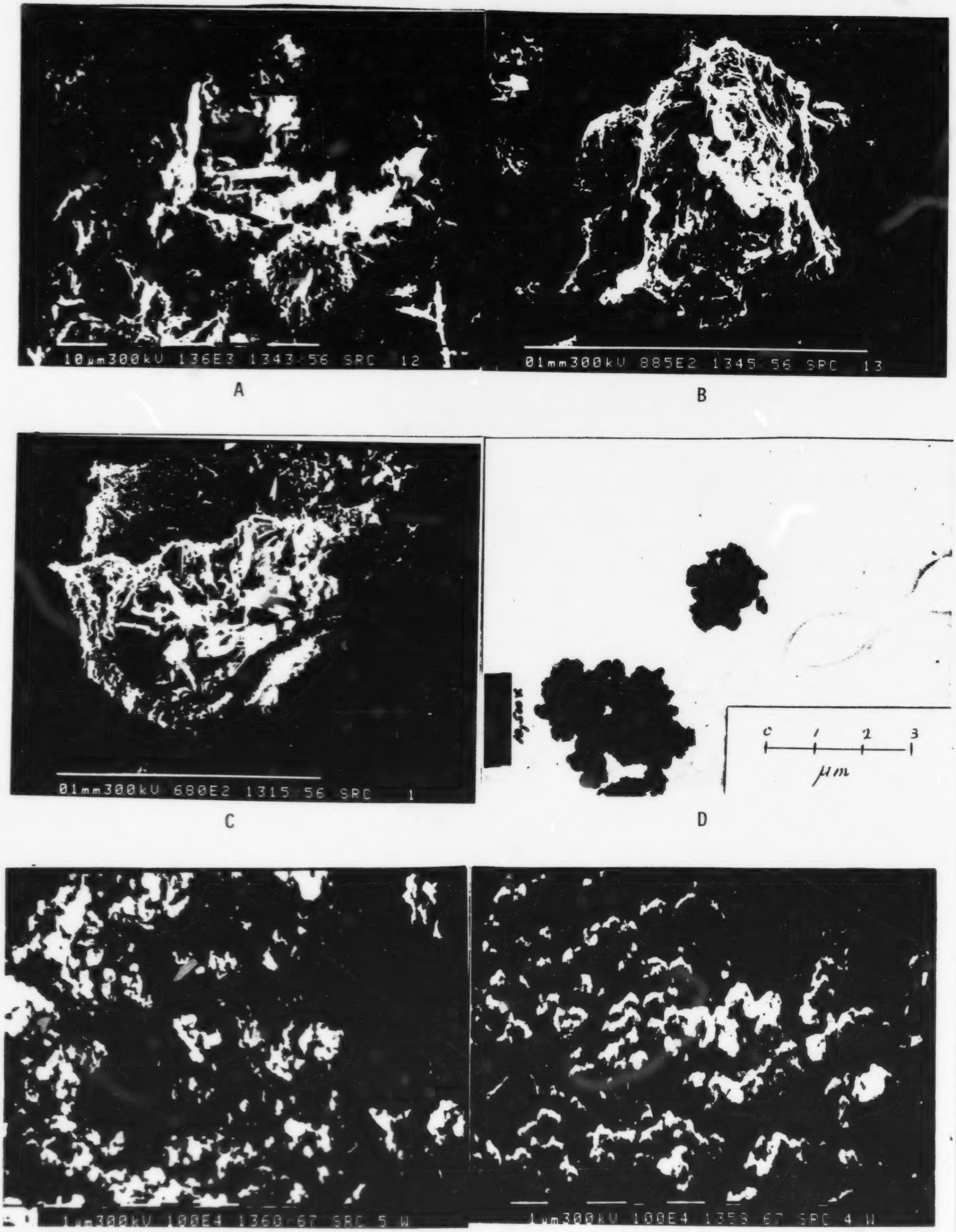
Figure 3B Precipitate No. 13. An irregular shaped grain of brucite $[Mg(OH)_2]$ (885 X).

Figure 3C Precipitate No. 1. Photo shows a ruptured pisolith exposing the core of gypsum crystals and pieces of the thin shell made up of fine grained crystals (680 X).

Figure 3D Several aggregates of sub-micron size crystals analysed by an EDAX system attached to a transmission electron microscope (TEM photo; 10,500 X).

Figure 3E Yellow-brown amorphous residue (No. 5W) obtained from Precipitate No. 5. The residue is composed of quite uniformly sized crystals about 0.1 to 0.3 um across. Several larger grains with a different morphology are present which may be residual gypsum. The amorphous residue appears to be composed of one crystal type (1000 X).

Figure 3F Yellow-brown amorphous residue (No. 4W) obtained from Precipitate No. 4. The description is the same as for Figure 3E, but the crystal size is somewhat larger: in the 0.5 um range. The large grain in the lower left portion of the photo may be residual gypsum (1000 X).


10µm300kV 136E3 1343 56 SRC 12
A
01mm300kV 885E2 1345 56 SRC 13
B
01mm300kV 680E2 1315 56 SRC 1
C
c
1
2
3
µm
D
1µm300kV 100E4 1360 67 SRC 5 W
E
1µm300kV 100E4 1353 67 SRC 4 W
F

FIGURES 3A TO 3F

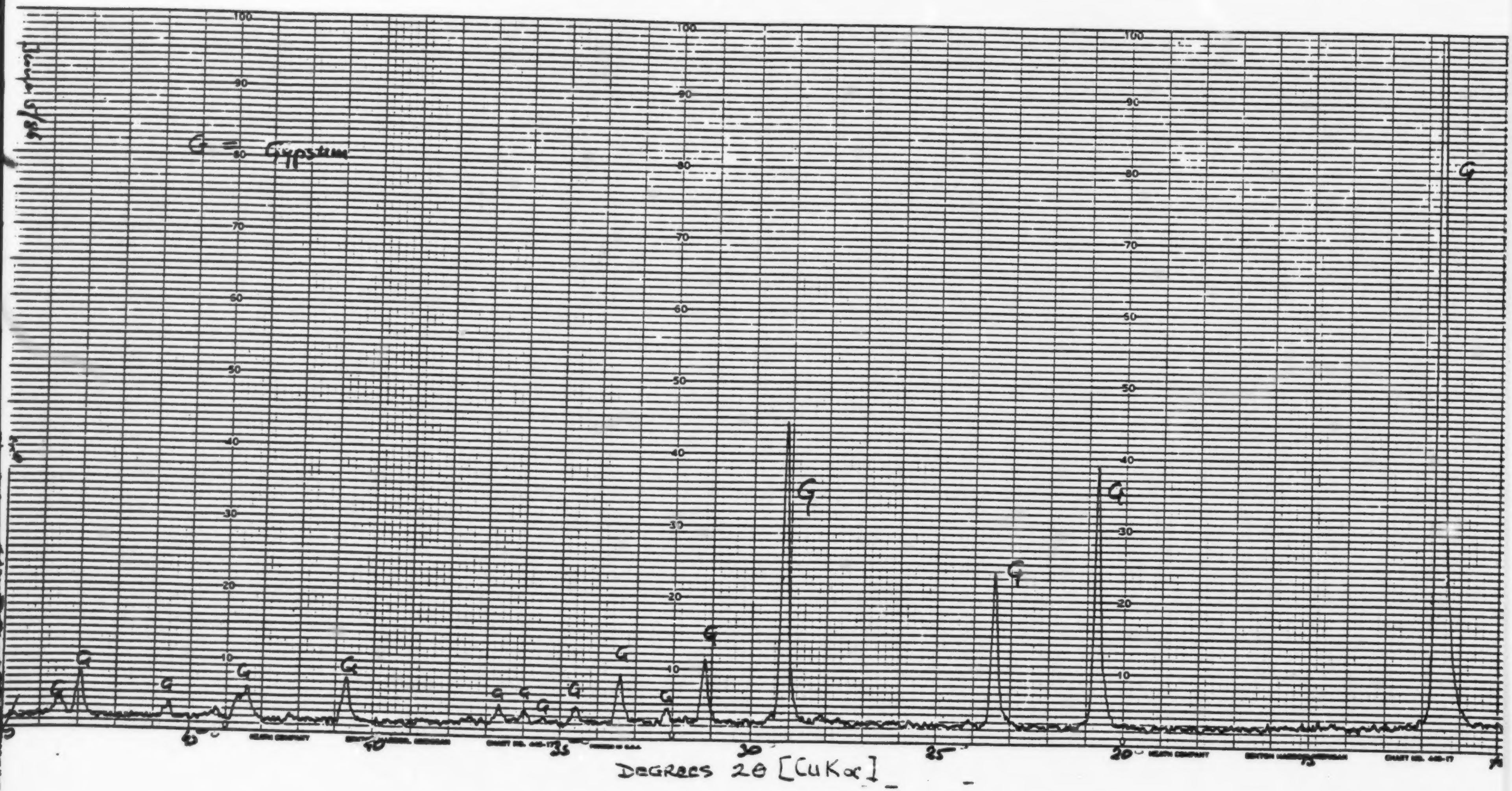


Figure 4. X-ray diffraction chart for Precipitate No. 1 showing the presence of only gypsum. The charts for Precipitates No. 2 to No. 12 were the same as for Precipitate No. 1.

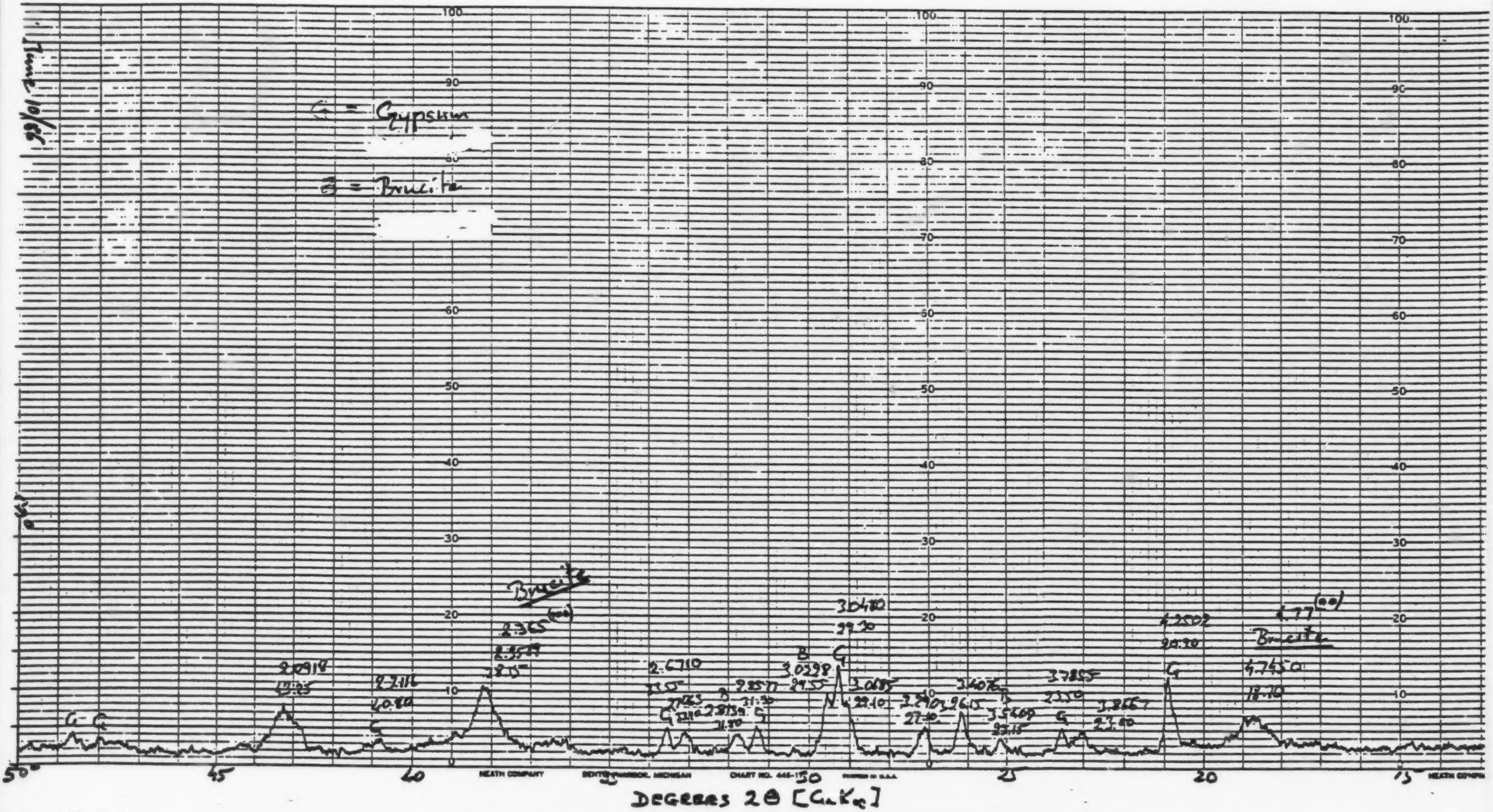
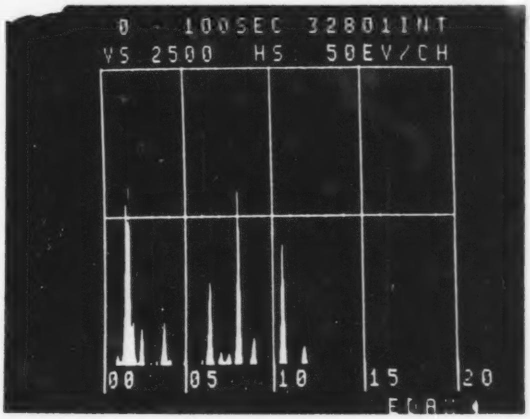


Figure 5. X-ray diffraction chart for Precipitate No. 13 showing two diffraction peaks of brucite (magnesium hydroxide) and many peaks of gypsum.

```
 ENTR  MEM: A #SAMPLE 1
* LIST  MEM: A SAMPLE 1
     .818        379. #
    1.325       5011. #-As  Lα
    1.499       5521. #-Al  Kα
    1.758       1644. #-Si  Kα
    2.323       1204. #-S   Kα
    2.700         35. #
    2.911        121. #
    3.271        190. #
    3.705       1347. #-Ca Kα
    4.077        192. #
    4.400         27. #
    4.605         20. #
    4.926        142. #
    5.425         12. #
    5.564         43. #
    5.969        145. #
    6.411       2522. #- Fe Kα
    7.032        424. #- Fe KB
    7.505        452. # Ni Kα

    8.495         90. #

    9.475          8. #
    9.575         11. #
    9.700         21. #
   10.071         52. #
   10.529       3797. # As - Kα
   11.265         38.
   11.724        620. # ———— As - KB
   12.129         14. #
   12.650          5. #
   13.475          9. #
   13.975          2. #
(WAVELENGTH)  (COUNTS)   (ELEMENT LINE)
              2/minutes.
```



```
 1
* ENTR  MEM: C #SAMPLE 4-1
* LIST  MEM: C SAMPLE 4-1
     .847        780. # Ni L Lβ
    1.321       2320. # As Lα
    1.473       1592. # Al Kα
    1.754       2664. # Si Kα
    2.327       1346. # S Kα
    2.692         95. #
    2.923        131. #
    3.239        279. #
    3.704       3712. # Ca Kα
    4.031        529. # Ca Kβ
    4.400          7. #
    4.925         43.
    5.645         85. #
    5.957        136. #
    6.409       3259. # Fe Kα
    7.044        626. # Fe Kβ
    7.476       4214. # Ni Kα


    9.300          1. #
    9.730         16. #
   10.075         61. #
   10.523       1419. # As Kα
   11.721        211. # As Kβ
   13.287          9. #
   17.550          8. #
   19.400          1. #
```

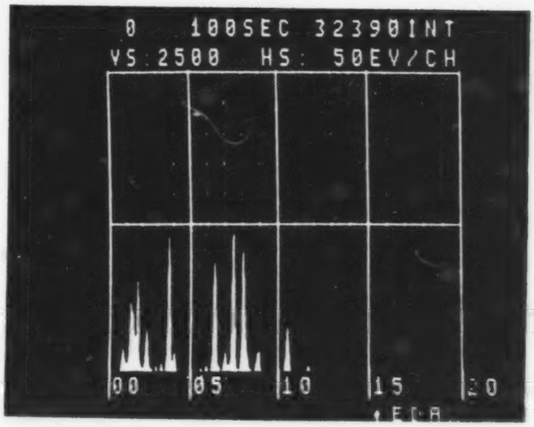


Figure 6. Results of the transmission electron microscope analyses on aggregates of sub-micron size tabular crystals in Precipitate No. 1 and No. 4. Both aggregates contain Si, Al, Fe, Ni and As. Aggregates in No. 1 contain high As and aggregates in No. 4 contain high Ni. Ca and S may be due to the presence of gypsum.

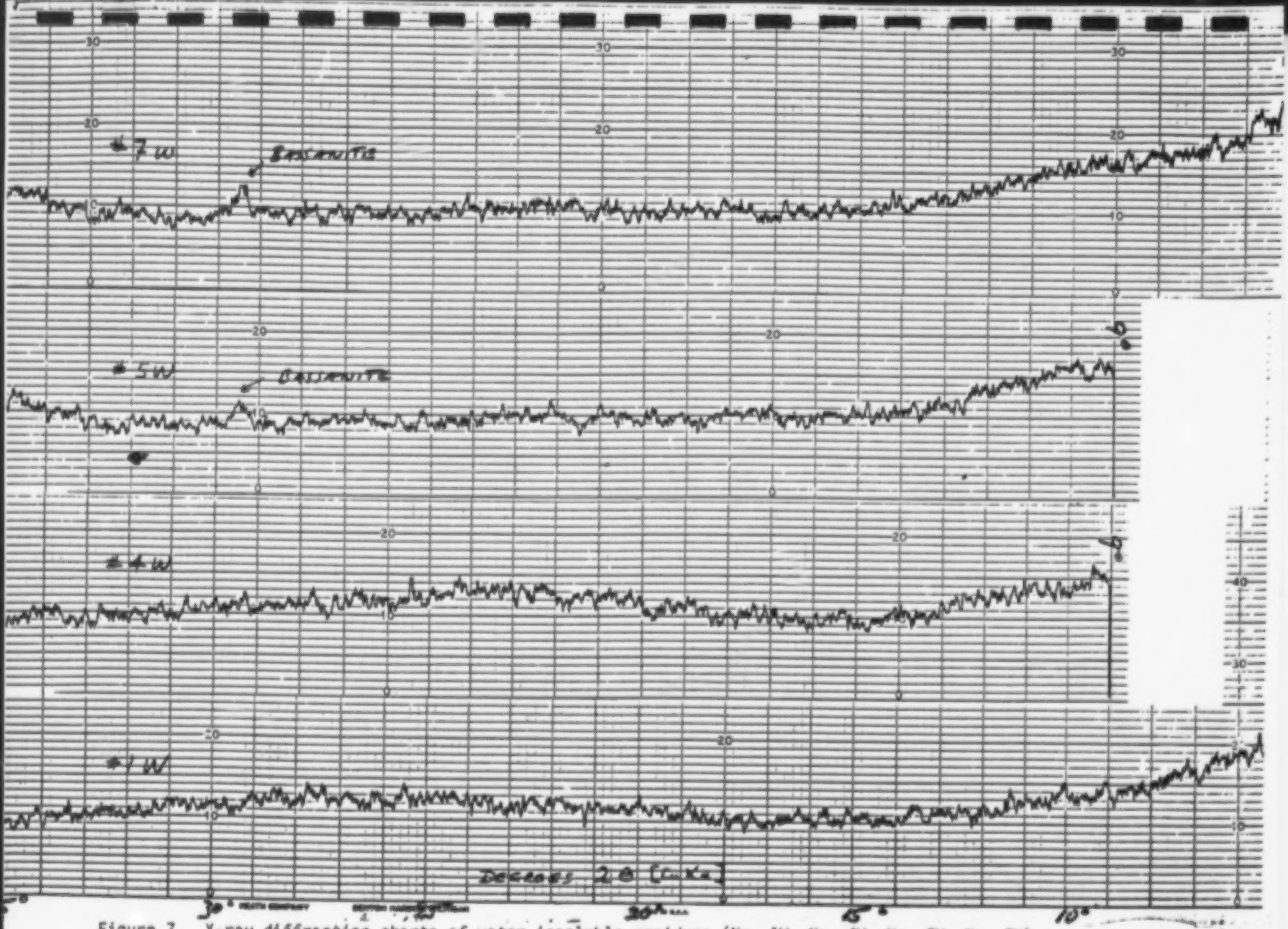


Figure 7. X-ray diffraction charts of water insoluble residues (No. 1W, No. 4W, No. 5W, No. 7W) after removal of gypsum by water leaching. Except for a residual bassanite peak, there are no diffraction peaks indicating that the residues are amorphous.

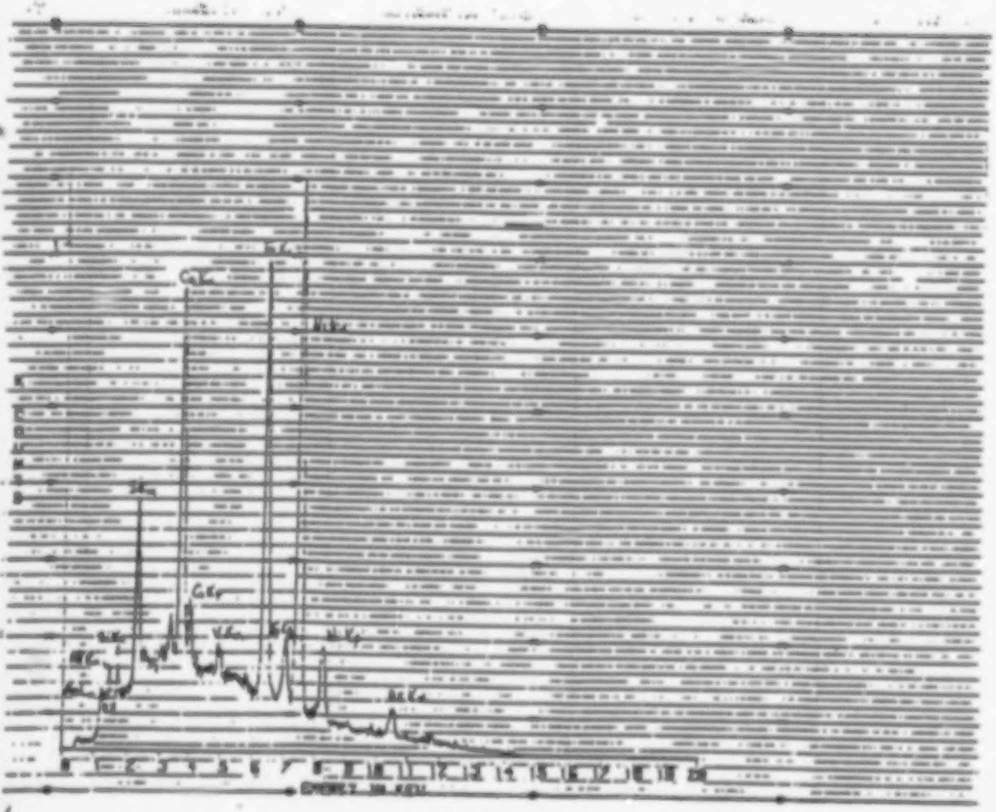


Figure 8A

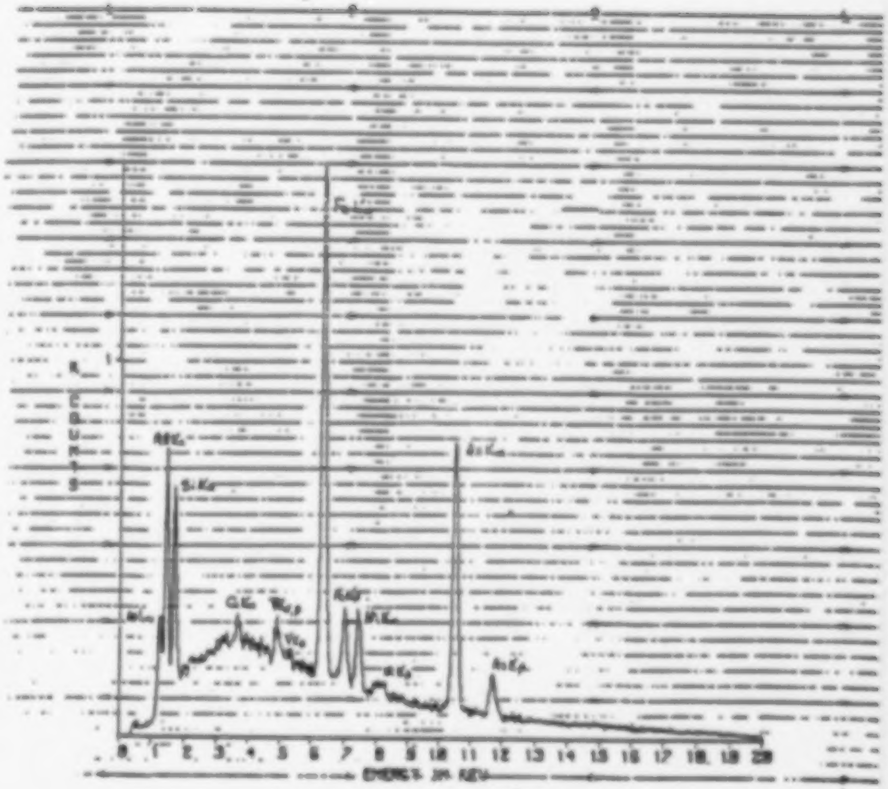


Figure 8B

Figure 8A. Electron microprobe results for Precipitate No. 2 showing that it contains Al, Si, Fe, Ni, As and V. Counts indicate that Ni>Fe>As. Ca and S are probably due to gypsum.

Figure 8B. Electron microprobe results for residue No. 1W showing significant concentrations of Al, Si, Fe, Ni, As and some Ca and V. Based on uncorrected counts Fe>As>Ni.

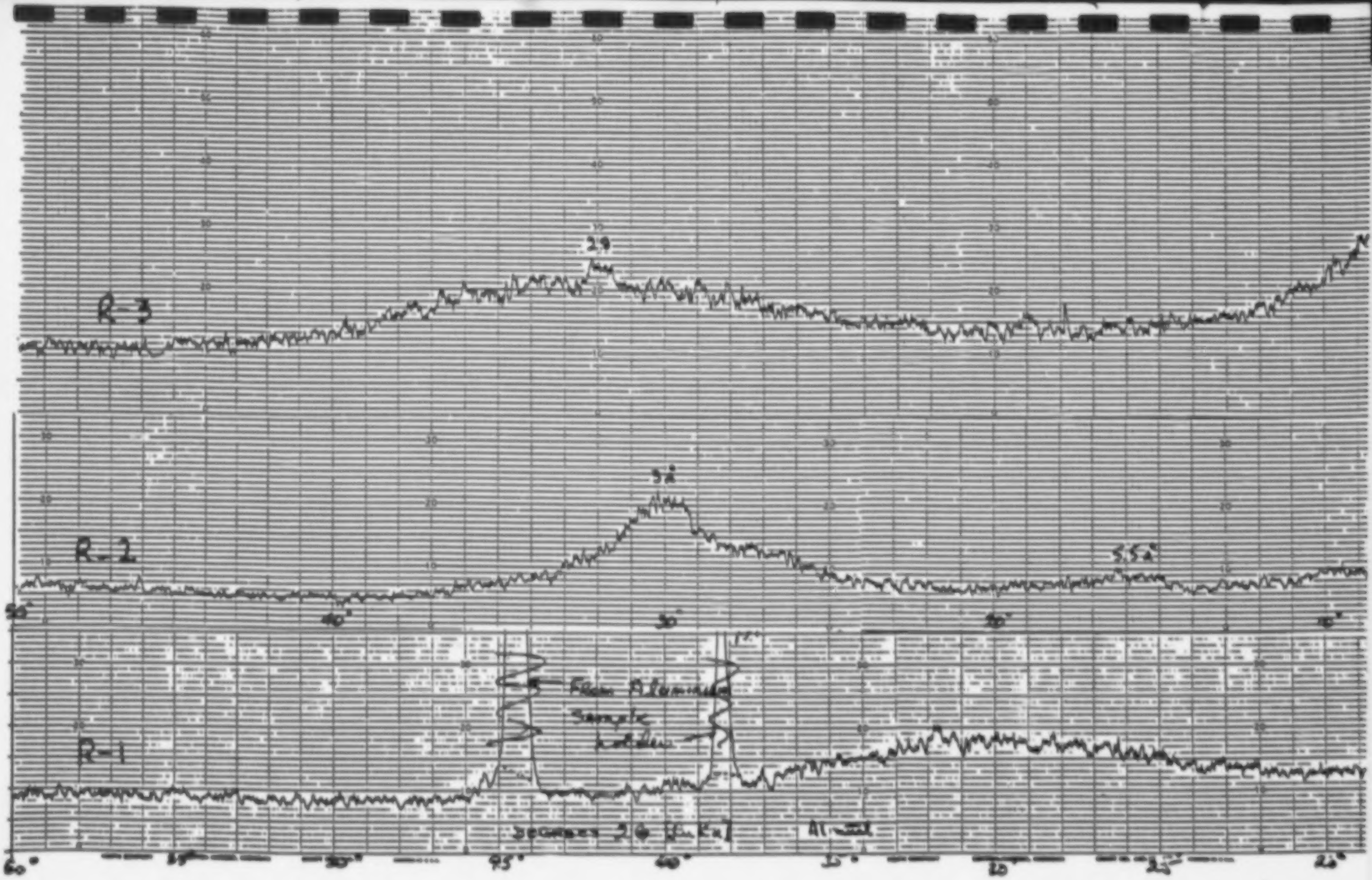


Figure [illegible]. X-ray diffraction charts for synthetic reference standards R-1, R-2, R-3 indicating that they are generally amorphous.

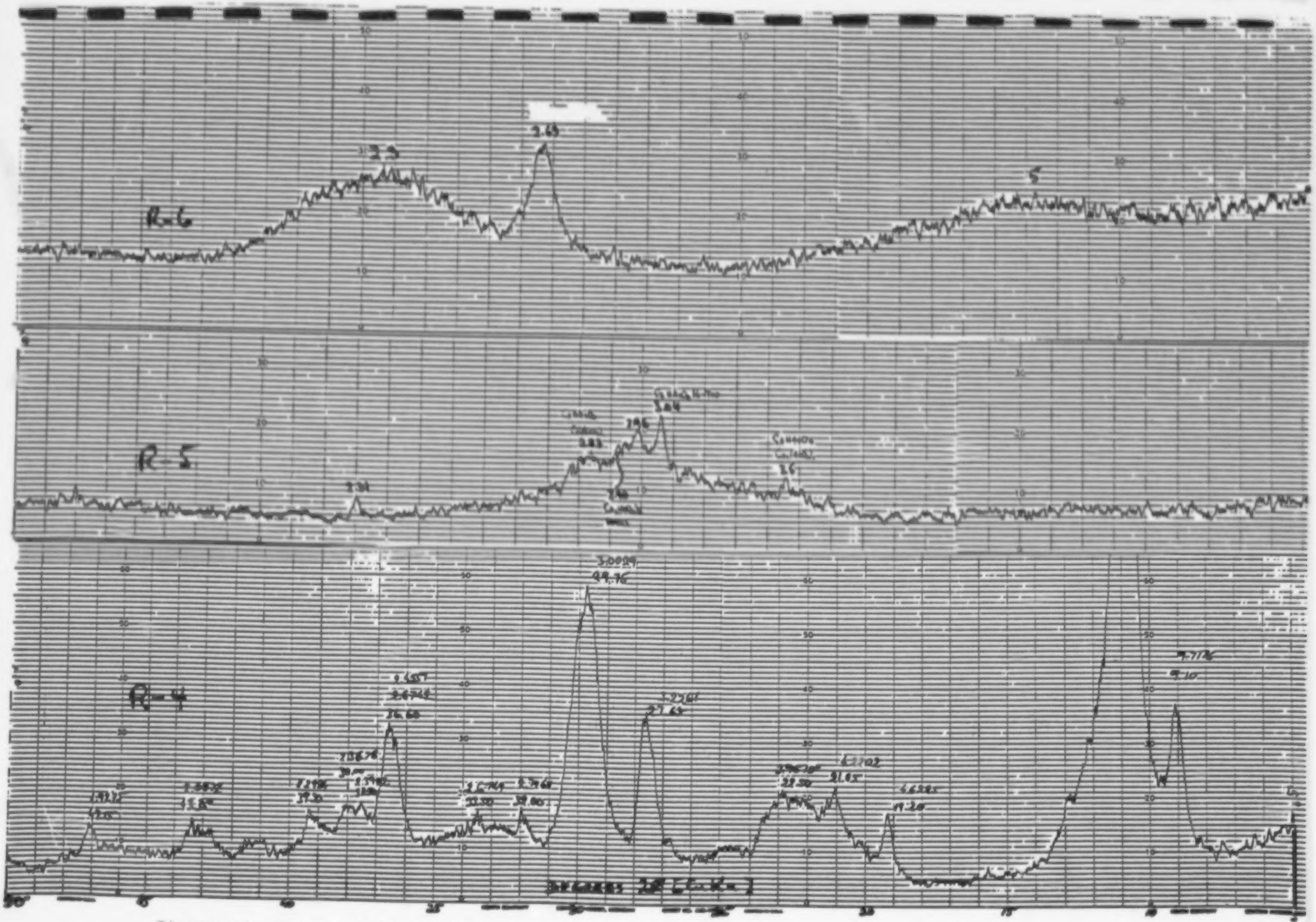


Figure 10. X-ray diffraction charts for synthetic reference standards R-4, R-5, R-6. R-4 is apparently crystalline but the peaks could not be identified.

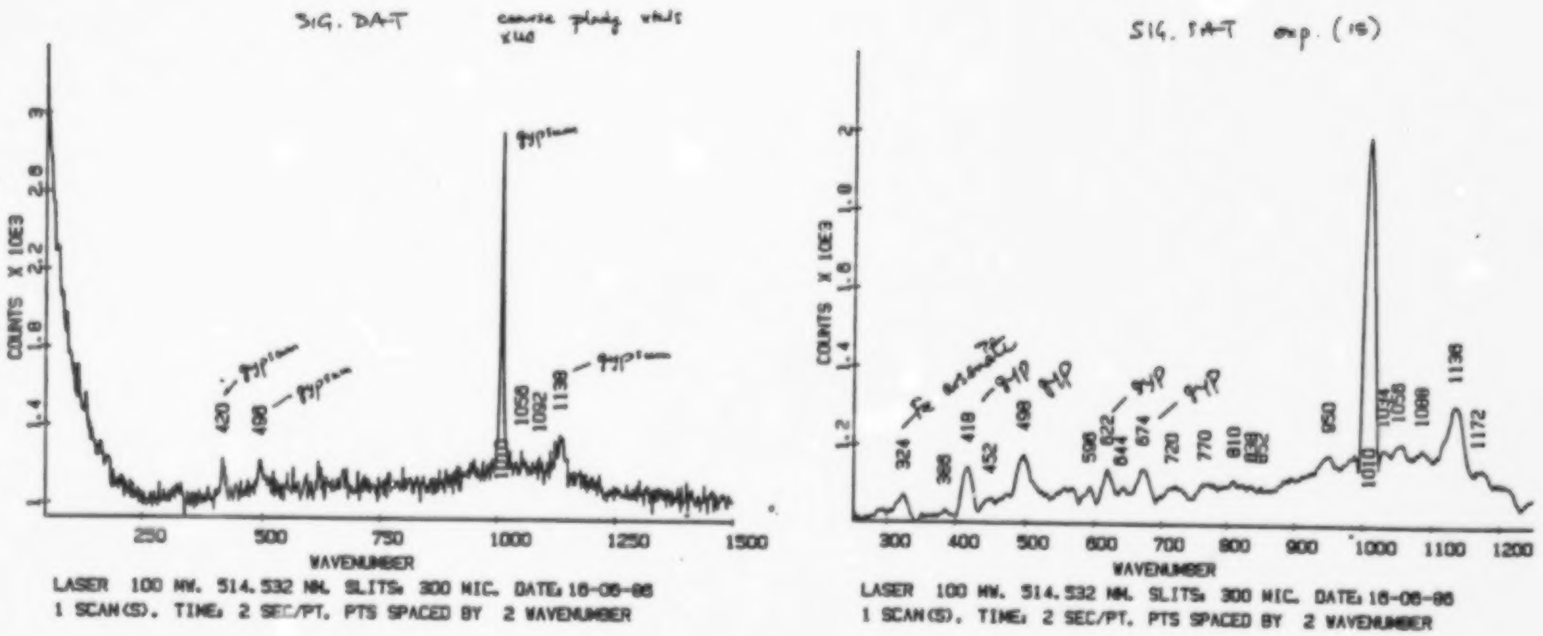


Figure 11. Raman microprobe scans of Precipitate No. 1 showing the Raman bands of gypsum and one weak Raman band of Fe arsenate at 324 cm-1.

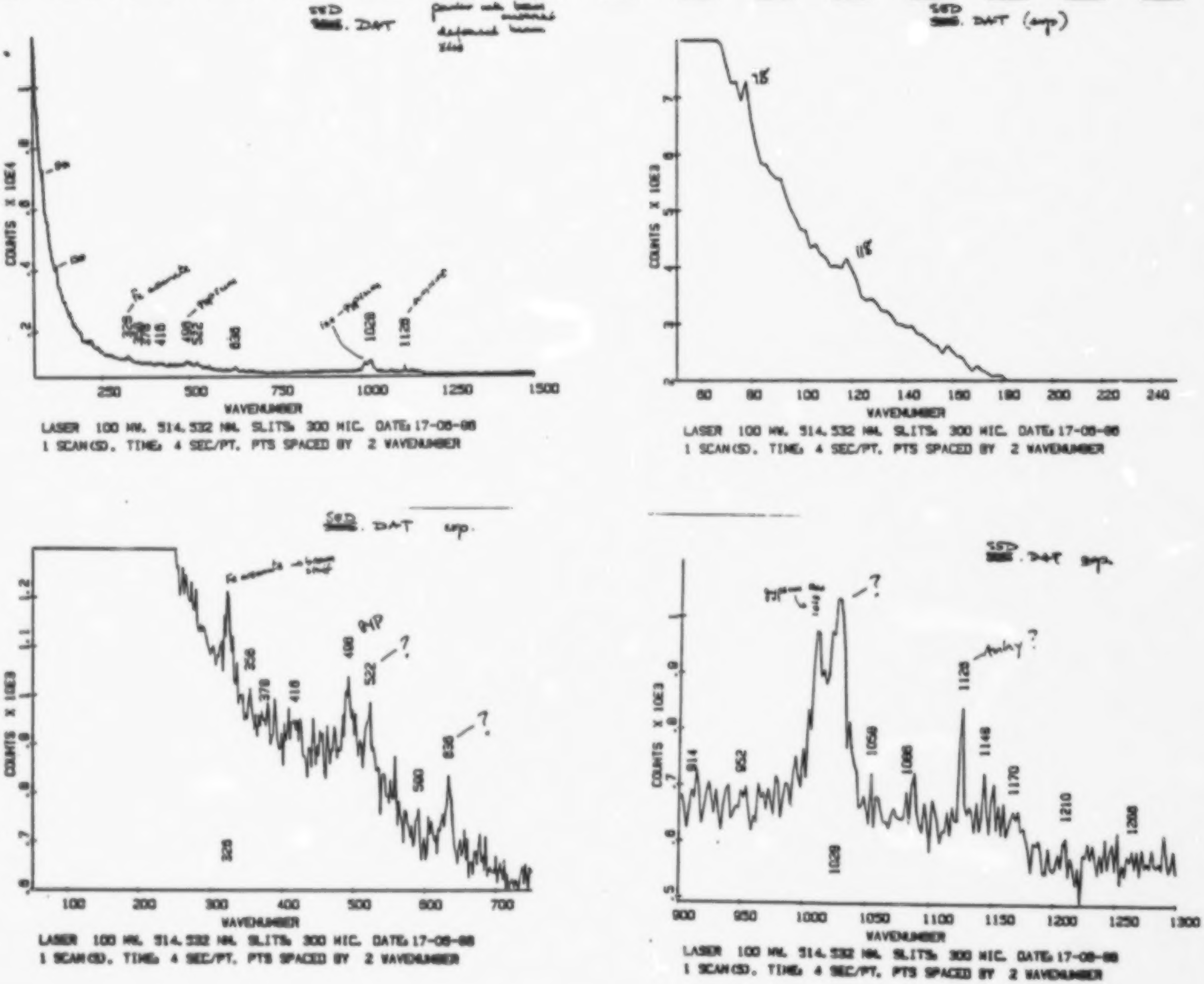
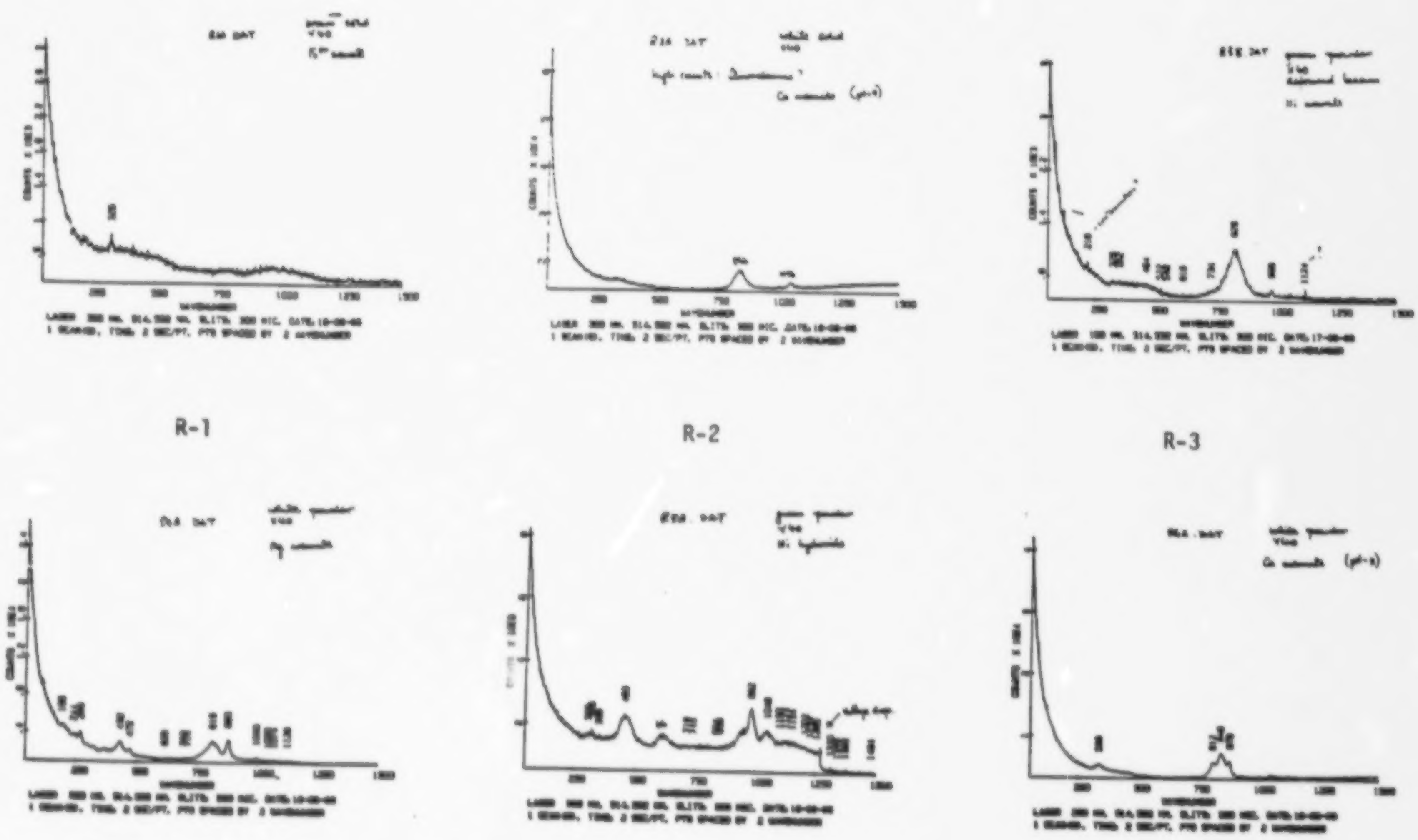


Figure 12. Raman microprobe scans of Precipitate No. 5 showing Raman bands of gypsum and one weak Raman band of Fe arsenate at 326 cm-1.



R-1

R-2

R-3

R-4

R-5

R-6

Figure 13. Raman bands for the six synthetic reference standards.

APPENDIX C

PREPARATION OF STANDARDS FOR RAMAN SPECTROSCOPY

APPENDIX C

PREPARATION OF STANDARDS FOR RAMAN SPECTROSCOPY

The following standard preparations were required for Raman spectroscopy work:

- calcium arsenate precipitated at pH 5
- calcium arsenate precipitated at pH 9
- calcium arsenate precipitated at pH 11
- magnesium arsenate precipitated at pH 9
- ferric arsenate precipitated at pH 5
- nickel arsenate precipitated at pH 5
- nickel arsenate precipitated at pH 9
- nickel hydroxide precipitated at pH 9

Calcium arsenate-pH 5

8.3 g $Na_2HAsO_4.7H_2O$ (2.5 g As) was dissolved in 900 mL of water. The initial pH was 8.7 and this was brought to 5.0 with 115 ml of 50 g/L HNO_3. To this was added a solution of 15.3 $Ca(NO_3)_2.4H_2O$ (2.6 g Ca) in 100 ml H_2O with continuous mixing. The pH was kept at 5 for 1 hour. No precipitate was observed. Temperature was 28°C.

Calcium arsenate-pH 9 (Reference Standard R-2)

The same procedure was used, other than the neutralization pH which was 9.0. It took two drops 40 g/L NaOH to bring the pH of the arsenate solution to 9.0. When the calcium nitrate solution was added, the solution pH went to 7.8 and it took 22 mL 1N NaOH to bring it up to 9. A milky colloidal-looking precipitate was obtained which filtered easily to yield a white translucent filter cake. This was dried at 55°C in an air current to give 6.3 g of sample R-2, a white solid with occasional creamcolored translucent margins or streaks.

Calcium arsenate-pH 11 (Reference Standard R-6)

The procedure was as before except with a target pH of 11 it took 10 mL 50 g/L NaOH to bring the arsenate solution to pH 11 before adding the calcium ion and 26 more mL of NaOH after the calcium addition. A similar filter cake to R-2 produced white angular chunks looking like laundry starch. This precipitate weighed 7.7 g.

Magnesium arsenate-pH 9 (Reference Standard R-4)

A similar procedure was used except that the calcium salt was replaced by 12.1 g $MgSO_4.7H_2O$ (1.2 g Mg). It took 0.5 mL NaOH to bring the solution to pH 9 before adding the magnesium sulfate and 20 mL NaOH thereafter. The filter cake, after drying under an air current at room temperature, weighed 5.5 g. This was sample R-4, a brilliantly white precipitate of earthy texture.

Ferric arsenate-pH 5 (Reference Standard R-1)

Here 8.3 g of Na_2HAsO_4 was mechanically stirred to dissolve it in 900 mL of water. The solution was taken down to pH 2.3 with 51 mL of 50 g/L HNO_3 from its original pH of 8.6 in order to be sure that the iron salt would not singly hydrolyze to $Fe(OH)_3$ at that pH. 13.1 g $FeCl_3.6H_2O$ (2.7 g Fe) dissolved in 100 mL of water was then added. The pH went down to 1.45 and a precipitate fell out, or at least the solution went yellowish and opaque. Caustic solution was added to adjust the pH to 5. The precipitate turned reddish.

The mixture was stirred for an hour and filtered. It filtered very slowly with four Buchner filtrations being run in parallel to filter only 1 L of dilute pulp.

After drying in an air current at room temperature 10.4 g of solid R1, a brown precipitate with a faint red tinge and the texture of chalcedonic silica, was obtained.

Nickel arsenate-pH 5

Here the procedure was much the same as the pH 5 Calcium Arsenate test, except that the precipitating agent was 13.4 g $NiSO_4.5H_2O$ (3.0 g Ni) dissolved in 100 mL H_2O. There was the usual pH adjustment to 5 both before and after the addition of the nickel salt. No precipitate was formed.

Nickel arsenate-pH 9 (Reference Standard R-3)

The procedure was the same as above, but the target pH was 9. This precipitate needed a close filter paper, #50, to retain it. After drying under an air current at room temperature 9.0 g of sample R3, a light green material of earthy texture, was obtained.

Nickel hydroxide-pH 9 (Reference Standard R-5)

Here 13.4 g $NiSO_4.6H_2O$ (3 g Ni) were dissolved in 900 mL H_2O with stirring. It took 71 mL of 50 g/L NaOH to raise the pH from 6.3 to 9.1. After 1 hour of stirring, the pulp was filtered, with a close filter paper. After the usual drying 5.8 g of sample R5, deep green transparent glassy shards, plainly a xerogel, were obtained.